PILOT- AND FULL-SCALE DEMONSTRATION OF ADVANCED MERCURY CONTROL TECHNOLOGIES FOR LIGNITE-FIRED POWER PLANTS

Final Report

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PILOT- AND FULL-SCALE DEMONSTRATION OF ADVANCED MERCURY CONTROL TECHNOLOGIES FOR LIGNITE-FIRED POWER PLANTS

ABSTRACT

The overall objective of the project was to develop advanced innovative mercury control technologies to reduce mercury emissions by 50%–90% in flue gases typically found in North Dakota lignite-fired power plants at costs from one-half to three-quarters of current estimated costs. Power plants firing North Dakota lignite produce flue gases that contain >85% elemental mercury, which is difficult to collect. The specific objectives were focused on determining the feasibility of the following technologies: Hg oxidation for increased Hg capture in dry scrubbers, incorporation of additives and technologies that enhance Hg sorbent effectiveness in electrostatic precipitators (ESPs) and baghouses, the use of amended silicates in lignite-derived flue gases for Hg capture, and the use of Hg adsorbents within a baghouse. The approach to developing Hg control technologies for North Dakota lignites involved examining the feasibility of the following technologies: Hg capture upstream of an ESP using sorbent enhancement, Hg oxidation and control using dry scrubbers, enhanced oxidation at a full-scale power plant using tire-derived fuel and oxidizing catalysts, and testing of Hg control technologies in the *Advanced Hybrid™* filter.

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NOMENCLATURE

A/C	air to cloth
ACI	activated carbon injection
AHPC	advanced hybrid particulate collector
APCD	air pollution control device
ASTM	American Society for Testing and Materials
CEM	continuous emission monitor
CMM	continuous mercury monitor
DOE	U.S. Department of Energy
EERC	Energy & Environmental Research Center
EPA	U.S. Environmental Protection Agency
ESP	electrostatic precipitator
FF	fabric filter
FGD	flue gas desulfurization
Hg^0	elemental mercury
Hg^{2+}	oxidized mercury
Hg(g)	total gaseous mercury, includes Hg^0 and Hg^{2+}
Hg(p)	particulate-associated mercury
Hg(total)	total mercury, includes Hg^0, Hg^{2+}, and Hg(p)
ICR	Information Collection Request
ID	induced draft
LAC	lignite-based activated carbon
lb	pound
LOI	loss on ignition
Macf	million actual cubic feet (at 300°F)
µg	microgram
NETL	National Energy Technology Laboratory
Nm^3	dry normal cubic meter at (20°C, 1 atm)
OH	Ontario Hydro (as in the Ontario Hydro method, ASTM D6784-02)
pc	pulverized coal
PCD	particulate control device
PJBH	pulse-jet baghouse
ppm	parts per million
PRB	Powder River Basin
PTC	particulate test combustor
PTFE	polytetrafluoroethylene
QA/QC	quality assurance/quality control
SCR	selective catalytic reduction
SDA	spray dryer absorber
SEA	sorbent enhancement additive
TDF	tire-derived fuel

PILOT- AND FULL-SCALE DEMONSTRATION OF ADVANCED MERCURY CONTROL TECHNOLOGIES FOR LIGNITE-FIRED POWER PLANTS

EXECUTIVE SUMMARY

North Dakota lignite-fired power plants have shown a limited ability to control mercury emissions in currently installed electrostatic precipitators (ESPs), dry scrubbers, and wet scrubbers. This low level of control can be attributed to the high proportions of Hg^0 present in the flue gas. Speciation of Hg in flue gases analyzed as part of the U.S. Environmental Protection Agency information collection request for Hg data showed that Hg^0 ranged from 56% to 96% and oxidized mercury ranged from 4% to 44%. The Hg emitted from power plants firing North Dakota lignites ranged from 45% to 91% of the total Hg, with the emitted Hg being greater than 85% elemental. The higher levels of oxidized mercury were only found in a fluidized-bed combustion system, which had high levels of carbon in the ash that captured Hg(g). Typically, the form of Hg in the pulverized coal (pc)- and cyclone-fired units was dominated by Hg^0 at greater than 85%, and the average amount of Hg^0 emitted from North Dakota power plants was 6.7 lb/TBtu.

The goal of this Energy & Environmental Research Center (EERC) project was to develop and evaluate advanced and innovative concepts for controlling Hg emissions from North Dakota lignite-fired power plants by 50%–90% at costs of one-half to three-quarters of current estimated costs. The specific objectives were focused on determining the feasibility of the following technologies: Hg oxidation for increased Hg capture in dry scrubbers, incorporation of additives and technologies that enhance Hg sorbent effectiveness in ESPs and baghouses, the use of amended silicates in lignite-derived flue gases for Hg capture, and the use of Hg adsorbents within a baghouse. The scientific approach to solving the problems associated with controlling Hg emissions from lignite-fired power plants involves conducting testing of the following processes and technologies that have shown promise on a bench, pilot, or field scale: 1) activated carbon injection upstream of an ESP combined with sorbent enhancement, 2) Hg oxidation and control using dry scrubbers, 3) enhanced oxidation at a full-scale power plant using tire-derived fuel (TDF) and oxidizing catalysts, and 4) testing of Hg control technologies in the *Advanced Hybrid™* filter insert.

Task 1 – Mercury Control Enhancement for Unscrubbed Systems Equipped with ESPs

A 550,000-Btu/hr pc-fired unit equipped with an ESP, known as the particulate test combustor (PTC), was used to fire lignites and test mercury control options in an unscrubbed system equipped with an ESP. Pilot-scale tests were performed using sorbent injections and mercury oxidation additives to evaluate their effectiveness on mercury emission control in a lignite-fired power system equipped with an ESP. The sorbents, including DARCO® FGD carbon, HCl-treated FGD carbon, EERC-treated FGD carbon, and ALSTOM-enhanced FGD carbon, were injected upstream of the ESP. The mercury oxidation additives or sorbent enhancement additives (SEAs) were introduced into the furnace with the coal to determine their

impacts on sorbent performance for mercury capture. The SEAs used include SEA1 and SEA2. SEA1 is a NaCl or $CaCl_2$ salt, and SEA2 is a proprietary EERC additive.

- The baseline test results show 88.2% of Hg^0, 10.9% of Hg^{2+}, and less than 1% of particulate-associated mercury in the Freedom lignite flue gas and virtually no mercury speciation change and inherent capture across the ESP.

- DARCO® FGD carbon injection can oxidize and capture mercury with 51.5% efficiency at 4.59 lb/Macf and reached 67.2% at the elevated 18.4 lb/Macf injection rate.

- Both mercury oxidants SEA1 (NaCl) and SEA2 have a positive mercury removal effect on the Freedom coal flue gas in the ESP configuration by enhancing mercury vapor reactivity with fly ash and in-flight DARCO® FGD carbon.

- Mercury removal efficiency reached 67.5% with 4.57 lb/Macf DARCO® FGD injection combined with 3.67 lb/Macf SEA1 (NaCl) injection, the same as the level achieved in the 18.4-lb/Macf DARCO® FGD carbon injection alone.

- SEA2 is three times as effective as SEA1 (NaCl) for enhancing reactivity between mercury vapor and fly ash and significantly improves DARCO® FGD performance for mercury capture, reaching 76.1% under 2.57 lb/Macf SEA2 injection rate in combination with the 2.57-lb/Macf DARCO® FGD injection rate.

- The treated-FGD carbon greatly increased mercury removal efficiency in the Freedom lignite flue gas for the ESP configuration. Lower feed rates of the treated-FGD carbon were required to attain higher mercury collection efficiencies as compared to those observed with untreated DARCO® FGD sorbent.

- The ALSTOM sorbent performed very well in the ESP configuration, with one sorbent achieving over 90% mercury removal at an injection rate of <2 lb/Macf.

Task 2 – Mercury Oxidation Upstream of Dry Scrubbers

Three potential Hg sorbents (DARCO® FGD, Amended Silicate™, and EERC-treated FGD) and three Hg^0 oxidation and sorbent enhancement additives (SEA1 [NaCl, $CaCl_2$] and SEA2) to improve the Hg(g) removal efficiency were evaluated in the PTC equipped with a spray dryer adsorber (SDA)–fabric filter (FF). A Center lignite coal was burned in the unit while Hg(g) concentrations were measured using CMMs at the SDA inlet and FF outlet to evaluate Hg removal performance.

- Using the Hg and Cl contents of the Center lignite, the levels in the combustion flue gas were calculated to be 13.8 µg/Nm^3 and 1.59 ppmv, respectively (on a dry flue gas at 3.0% O_2 basis). The baseline measured values determined using standard methods and continuous mercury monitoring ranged from 12 to 13 µg/Nm^3 at the SDA–FF inlet. The initial baseline removal of mercury without additives or sorbents was found to be 2.5%. Testing at a later

time during the SDA–FF testing showed higher baseline removal rates of up to 18% because of residual oxidants or sorbents that were difficult to remove from the FF.

- Mercury Sorbent Performance

  - DARCO® FGD Activated Carbon. The Hg(g) removal efficiency when injecting activated carbon upstream of the SDA improved with increasing injection rates until it approached about 60% at an injection rate of 7.35 lb/Macf.

  - EERC-Treated FGD. The EERC-treated FGD provided very good Hg(g) capture even at a low injection rate of 1.84 lb/Macf of over 80%. Increasing the injection rate to 3.67 lb/Macf slightly improved SDA–FF Hg(g) capture.

  - Amended Silicate™. Hg(g) removal efficiencies during Amended Silicate™ injection averaged 74.9% and were highly variable as evidenced by a 95% confidence limit of ±9.1%. The effectiveness of Amended Silicate™ to capture Hg(g) was probably enhanced by the presence of residual Cl in the system. After the injection of Amended Silicate™, the SDA–FF Hg(g) removal efficiency gradually returned to the level attained prior to testing the Amended Silicate™.

- Hg^0 Oxidation and Sorbent Enhancement Additive Performance

  - SEA1 (NaCl). The addition of NaCl to the Center lignite did not significantly increase the level of oxidized mercury. The removal efficiency across the SDA–FF was 23.5% with 3.67 lb/Macf of NaCl added and increased to 27.8% with 11 lb/Macf.

  - SEA1 (NaCl) and DARCO® FGD. For injection of 3.67 lb/Macf of NaCl into the Center lignite coal and DARCO® FGD into combustion flue gas, the Hg(g) capture and subsequent SDA–FF removal efficiency was found to be 70%. Increasing the level of NaCl up to 11 lb/Macf and keeping the DARCO® FGD constant, the removal efficiency approached 90%. The combination of NaCl addition and DARCO® FGD injection is very effective in capturing Hg(g) in the SDA–FF pollution control devices.

  - SEA1 ($CaCl_2$). The $CaCl_2$ additions alone caused Hg(g) and Hg^0 levels to gradually decline from over 14 to 8.3 μg/Nm^3 with increasing $CaCl_2$ addition rates with up to 11 lb/Macf.

  - SEA1 ($CaCl_2$) and DARCO® FGD. Injection of DARCO® FGD at a rate of 3.67 lb/Macf with 11 lb/Macf $CaCl_2$ addition to the coal resulted in 80% Hg(g) removal across the SDA–FF. The SDA–FF Hg(g) removal efficiencies observed clearly demonstrate that the combination of $CaCl_2$ addition and DARCO® FGD injection provides much more effective Hg(g) emission control relative to $CaCl_2$ addition or DARCO® FGD injection alone.

  - SEA2. The addition of SEA2 alone to the coal at a rate of 3.67 lb/Macf resulted in about 80% removal across the SDA–FF.

– SEA2 and DARCO® FGD. The combination of DARCO® FGD injection at 1.84 lb/Macf and SEA2 addition provided exceptional SDA–FF Hg(g) capture, >90%, even at the lower addition rate of 1.84 lb/Macf.

Task 3 – Field Tests to Determine Impacts of Oxidizing Agents on Mercury Speciation

Ontario Hydro Hg measurements were taken at the inlet and outlet of the ESP at the Heskett Station, with and without cofiring TDF. Approximately 100 tons of TDF was delivered from Auburndale Recycling and fired at a level of 10% on a heat basis. The TDF had a heating value of over 15,000 Btu/lb and contained 324 ppm chlorine. The amount of Hg removed increased from 50% without TDF to 80% while firing TDF. The chlorine added by the TDF is likely responsible for the increase in Hg capture. Flue gas chlorine measurements taken during the same sampling period indicated that the level of chlorine in the flue gas was higher without TDF. This may indicate that the extra chlorine was captured by calcium compounds that are present in the fly ash or bed material. More work should be conducted to support or disprove this hypothesis.

Previous studies conducted with selective catalytic reduction (SCR) catalysts on lignite-fired systems indicate that oxidation of Hg across an SCR is challenging. Other research has shown that specific metal oxides of vanadium and titanium are responsible for Hg oxidation across SCR catalysts. However, the oxidation of Hg will be highly dependent on the coal that is being fired. Heavy metal oxidation catalysts have also been studied downstream of an ESP. The results of this study indicate that palladium- and carbon-derived catalysts oxidized 65% and 80% of the Hg after 20 months and 13 months, respectively.

Task 4 – Particulate and Mercury Control for North Dakota Lignites Using the *Advanced Hybrid*™ Filter Technology

Pilot-scale tests were performed using sorbent injection and mercury oxidant addition to evaluate their effectiveness on mercury emission control in a lignite-fired power system equipped with an ESP followed by an *Advanced Hybrid*™ filter. The sorbents including DARCO® FGD carbon and regenerated FGD carbon were injected upstream of the ESP in continuous and batch injection modes in a 300° and 400°F flue gas environment. Different additives were introduced into the furnace with the coal to examine their impacts on sorbent performance for mercury capture.

- The baseline test results show the mercury in the Freedom lignite flue gas to be 88.2% elemental (Hg^0), 10.9% oxidized (Hg^{2+}), and less than 1% particulate-associated mercury and virtually no inherent mercury capture across the retrofit *Advanced Hybrid*™ filter.

- At the injection rate of <2 lb/Macf of DARCO® FGD carbon, continuous and batch injection modes showed the same level of mercury capture, reaching approximately 50%–60% capture at 2.02 lb/Macf. For higher DARCO® FGD carbon injection rates of >4 lb/Macf, batch injection had a better mercury capture performance than the continuous mode since the DARCO® FGD carbon surface was more fully utilized.

- DARCO® FGD carbon showed no significant temperature dependence on mercury removal in the retrofit *Advanced Hybrid*™ filter.

- Both mercury oxidants NaCl and SEA2 have positive mercury removal effects in the Freedom coal flue gas in the *Advanced Hybrid*™ filter configuration by enhancing mercury vapor reactivity with fly ash. The addition of metallic zinc into the furnace was not effective in capturing mercury, and it deteriorated NaCl performance for mercury removal in the retrofit *Advanced Hybrid*™ filter.

- The combination of NaCl–DARCO® FGD injection significantly improved mercury removal in the retrofit *Advanced Hybrid*™ filter by attaining higher mercury collection efficiency with reduced DARCO® FGD injection rate for both continuous and batch injections. Mercury collection efficiency reached 70.0% using 2.57 lb/Macf DARCO® FGD (continuous injection) combined with 3.67 lb/Macf NaCl injection, the same as the level achieved in the 8.08 lb/Macf DARCO® FGD carbon injection.

- The regenerated FGD carbon showed encouraging rates of effective mercury removal across the retrofit *Advanced Hybrid*™ filter with batch injection in 300°F flue gas environment, reaching 48% mercury collection at the 2.2-lb/Macf injection rate.

Task 5 – Field Testing of Sorbents

A trailer-mounted baghouse was successfully designed and constructed. The baghouse was mounted on a flatbed trailer for ease of transport and installation at any location. The slipstream baghouse chamber is designed to accommodate twelve 6-inch fabric filters, with bag lengths up to 12 feet. This equates to approximately 226 ft^2 of filtration area. To connect the slipstream baghouse to the required location at the boiler, two separate 10-inch flanges are required, one at the immediate inlet location and the other downstream of this location but upstream of any induced-draft fans.

The baghouse was successfully installed in slipstream fashion at Basin Electric's Leland Olds Station in April 2004. Two days of carbon injection testing was completed while burning North Dakota lignite coal. The highest Hg removal achieved was near 90% with 300 ppm Cl equivalent added to the coal and 2 lb/Macf DARCO® FGD carbon injected. The effect of face velocity on Hg removal was also tested. The results of this study indicate that a small increase in Hg removal is detected as the face velocity is increased; however, further testing should be done to determine if the effect is real. A residual removal effect was observed on Day 2. The Cl added to the coal on Day 1 seemed to enhance the removal of Hg well into the second day of testing.

PILOT- AND FULL-SCALE DEMONSTRATION OF ADVANCED MERCURY CONTROL TECHNOLOGIES FOR LIGNITE-FIRED POWER PLANTS

INTRODUCTION

North Dakota lignite-fired power plants have shown a limited ability to control mercury emissions in currently installed electrostatic precipitators (ESPs), dry scrubbers, and wet scrubbers (1). This low level of control can be attributed to the high proportions of Hg^0 present in the flue gas. Speciation of Hg in flue gases analyzed as part of the U.S. Environmental Protection Agency (EPA) information collection request (ICR) for Hg data showed that Hg^0 ranged from 56% to 96% and oxidized mercury ranged from 4% to 44%. The Hg emitted from power plants firing North Dakota lignites ranged from 45% to 91% of the total Hg entering the plant based on coal analysis, with the emitted Hg being greater than 85% elemental. The higher levels of oxidized and particulate mercury were only found in a fluidized-bed combustion system. The fluidized-bed system had high levels of carbon in the ash that captured Hg(g). Typically, the form of Hg in the pulverized coal (pc)- and cyclone-fired units was dominated by Hg^0 at greater than 85%, and the average amount of Hg^0 emitted from North Dakota power plants was 6.7 lb/TBtu (1, 2).

The overall goal of this project was to develop and evaluate advanced and innovative concepts for controlling Hg emissions from North Dakota lignite-fired power plants by 50%–90% at costs of one-half to three-quarters of current estimated costs. The scientific approach to solving the problems associated with controlling Hg emissions from lignite-fired power plants involves conducting testing of the following processes and technologies that have shown promise on a bench, pilot, or field scale: 1) activated carbon injection (ACI) upstream of an ESP combined with sorbent enhancement, 2) Hg oxidation and control using dry scrubbers, 3) enhanced oxidation at a full-scale power plant using tire-derived fuel (TDF) and oxidizing catalysts, and 4) testing of Hg control technologies in the *Advanced Hybrid™* filter insert.

This project was awarded under U.S. Department of Energy (DOE) National Energy Technology Laboratory (NETL) Cooperative Agreement No. DE-FC26-03NT41897. Because of the concern regarding anthropogenic release of mercury to the atmosphere and the lack of effective mercury control technologies available to meet likely future regulatory standards, the following organizations cosponsored the project: the North Dakota Industrial Commission; Minnkota Power Cooperative, Inc.; Basin Electric Power Cooperative; Otter Tail Power Company; Great River Energy; Montana–Dakota Utilities Co.; BNI Coal Ltd.; Dakota-Westmoreland, Inc.; and North American Coal Company. Equipment vendors including ADA Technologies Inc.; Haldor Topsoe Inc.; ALSTOM Power, Inc.; and Babcock & Wilcox Company participated in the program by providing materials and expertise to test their techniques. In order to meet the goal of the project, the primary objectives were focused on determining the feasibility of the following technologies: Hg oxidation for increased Hg capture in dry scrubbers, incorporation of additives and technologies that enhance Hg sorbent effectiveness in ESPs and baghouses, the use of amended silicates in lignite-derived flue gases for Hg capture, and the use of Hg adsorbents within a baghouse. The specific tasks for the project are summarized as follows.

Task 1 – Mercury Control Enhancement for Unscrubbed Systems Equipped with ESPs

This task evaluated technologies to control Hg emissions in lignite-fired power systems equipped with an ESP only, as well as provided valuable information for enhancing Hg control in other unscrubbed systems. Testing was performed using sorbent injection on the EERC's particulate test combustor (PTC) equipped with an ESP to evaluate Hg sorbent effectiveness in coal combustion flue gases.

Task 2 – Mercury Oxidation Upstream of Dry Scrubbers

Potential Hg^0 oxidation additives were evaluated using the PTC equipped with a spray dryer absorber (SDA). Pilot-scale testing involved a Center lignite coal with screening tests of several oxidation additives blended with the coals prior to injection into the furnace. Three sorbents were injected upstream of the SDA while burning Center lignite in the PTC. The most promising sorbents were also injected in combination with the oxidation additives to evaluate Hg capture performance.

Task 3 – Field Tests to Determine Impacts of Oxidizing Agents on Mercury Speciation

This task involved testing the ability of cofiring TDF with North Dakota lignite to increase the oxidized and particulate forms of mercury at a fluid bed-fired power plant (Montana–Dakota Utilities Heskett Station Unit 2, 85 MW, ESP). Testing included a baseline run firing 100% lignite at full load and up to 10% TDF (heating input basis). The second subtask involved a literature review and summary of the state of mercury oxidation catalysts in place of the proposed testing of a Hg oxidation agent in conjunction with a preexisting EERC project.

Task 4 – Particulate and Mercury Control for North Dakota Lignites Using the *Advanced Hybrid*™ Filter Technology

This task included reconfiguring the PTC with an ESP followed by the *Advanced Hybrid*™ filter system to simulate a full-scale retrofit system. Testing was performed using sorbent injection separately and in conjunction with furnace enhancements to evaluate Hg control effectiveness in coal combustion systems retrofitted with the *Advanced Hybrid*™ filter system.

Task 5 – Field Testing of Sorbents

This task evaluated how effectively Hg can be captured by using a sorbent-based technology in conjunction with a pulse-jet baghouse (PJBH) at a power plant in North Dakota. A portable baghouse was constructed, transported, and connected in slipstream fashion to a full-scale power plant for testing using actual flue gases. The proposed work plan initially included an evaluation of a Gore technology for mercury control; however, testing of the Gore technology was eliminated because of Gore's decision to abandon its mercury research program.

Task 6 – Project Reporting and Management

This task involved coordination of all testing conducted within the various tasks and subtasks of the project. Results of the research were presented in regular meetings with sponsors and project participants, quarterly reports, at conferences and scientific meetings, and in the final report.

BACKGROUND

The composition of a coal has a major impact on the quantity and form of Hg in the flue gas and, as a result, on the ability of air pollution control devices (APCDs) to remove Hg from flue gas. In general, North Dakota lignitic coals are unique because of a highly variable ash content, ash that is rich in alkali and alkaline-earth elements, high oxygen levels, high moisture levels, and low chlorine content. Although lignite and bituminous coals contain comparable levels of mercury, experimental results indicate that low-chlorine (<50-ppm) coal combustion flue gases (typical of North Dakota lignite) contain predominantly Hg^0, which is substantially more difficult to remove than Hg^{2+} (3). The generally high calcium contents of lignite coals may reduce the oxidizing effect of the already low chlorine content by reactively scavenging chlorine species (Cl, HCl, and Cl_2) from the combustion flue gas. The level of chlorine in flue gases of recently tested North Dakota and Saskatchewan lignites ranged from 2.6 to 3.4 ppmv, respectively, while chlorine contents in the coal on a dry basis, ranged from 11 to 18 ppmw, respectively.

Mercury Control Options

The technologies utilized for the control of Hg will ultimately depend upon the EPA-mandated emission limits. Options being investigated have the potential to attain between 50% and 90% control of Hg emissions. The Hg control strategies at North Dakota lignite-fired power plants involve, first, the enhancement of existing control technologies and, second, investigation and addition of additional control technologies. The strategies include sorbent injection with and without enhancements upstream of an ESP or fabric filter (FF) and Hg oxidation upstream of a wet or dry flue gas desulfurization (FGD) system. The new technologies being investigated include Hg capture using the EERC's advanced hybrid particulate collector (AHPC), or the *Advanced Hybrid*™ filter, and carbon beds (4).

Sorbent injection for removing Hg involves adsorption of Hg species by a solid sorbent injected upstream of a particulate control device such as an FF (baghouse) or ESP. Many potential Hg sorbents have been evaluated (4). These evaluations have demonstrated that the chemical speciation of Hg controls its capture mechanism and ultimate environmental fate.

ACI is the most mature technology available for Hg control. Activated carbons have the potential to effectively sorb Hg^0 and Hg^{2+} but depend upon the carbon characteristics and flue gas composition (4). Most activated carbon research has been performed in fixed-bed reactors that simulate relatively long-residence-time (gas–solid contact times of minutes or hours) Hg capture by a FF filter cake (5–7). However, it is important to investigate short-residence-time

(seconds) in-flight capture of Hg^0 because most of the coal-burning boilers in the United States employ cold-side ESPs for controlling particulate matter emissions. The projected annual cost for activated carbon adsorption of Hg in a duct injection system is significant. Carbon-to-mercury weight ratios of 3000:18,000 (lb carbon injected/lb Hg in flue gas) have been estimated to achieve 90% Hg removal from a coal combustion flue gas containing 10 μg/Nm^3 of Hg (8). More efficient carbon-based sorbents are required to enable lower carbon-to-mercury weight ratios to be used, thus reducing the costs. Recent testing conducted at the EERC illustrates the effectiveness of sorbents injected upstream of the ESP and baghouse.

EERC pilot-scale ESP and ESP–FF Hg removal efficiencies for the Fort Union lignite coals from Saskatchewan and North Dakota (Poplar River and Freedom coals) flue gases are compared in Figures 1 and 2 to those obtained at full-scale utility boilers where activated carbons were injected into a bituminous coal combustion flue gas upstream of a compact hybrid particulate collector (Toxecon™) (pulse-jet FF) and into bituminous and Powder River Basin (PRB) subbituminous coal combustion flue gases upstream of an ESP. Coal type (i.e., composition) is an important parameter that affects the Hg removal efficiency of a control device. During the pilot-scale lignite and utility-scale eastern bituminous coal tests, Hg removal efficiency increased with increasing ACI rates. Conversely, Hg removal efficiency was never greater than 70%, regardless of the ACI rate into the PRB subbituminous coal combustion flue gas. This limitation is probably caused by the low amount of acidic flue gas constituents, such as HCl, that promote Hg–activated carbon reactivity.
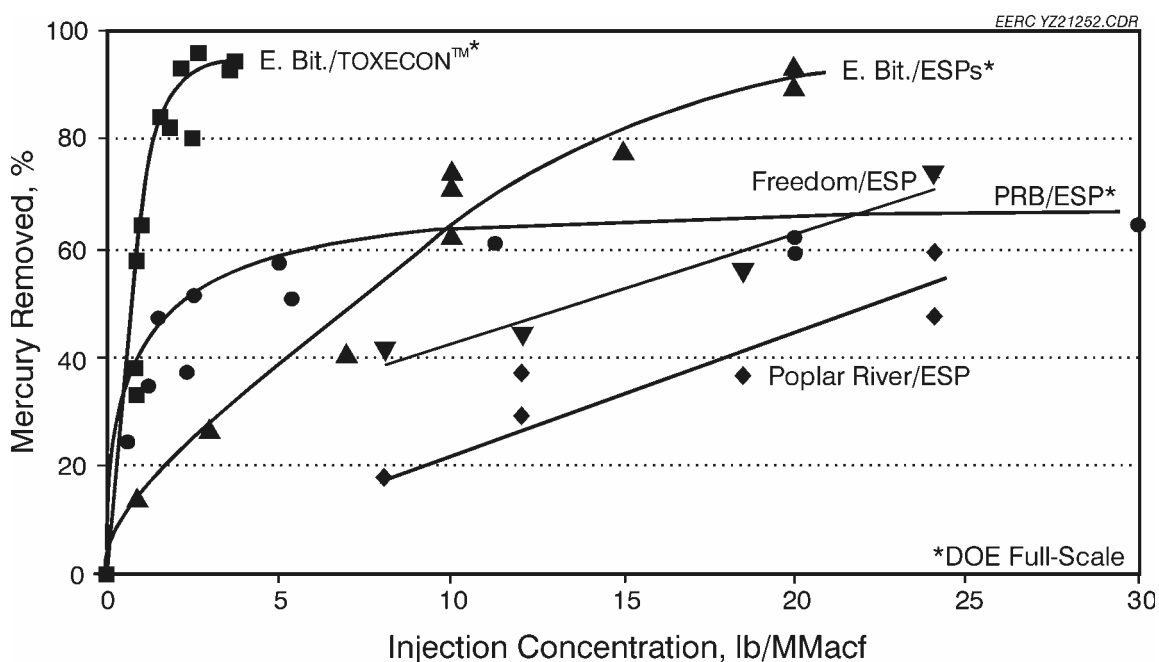
Figure 1. Pilot-scale ESP (8) and full-scale Toxecon™ and ESP (9) Hg removal efficiencies as a function of ACI rate.
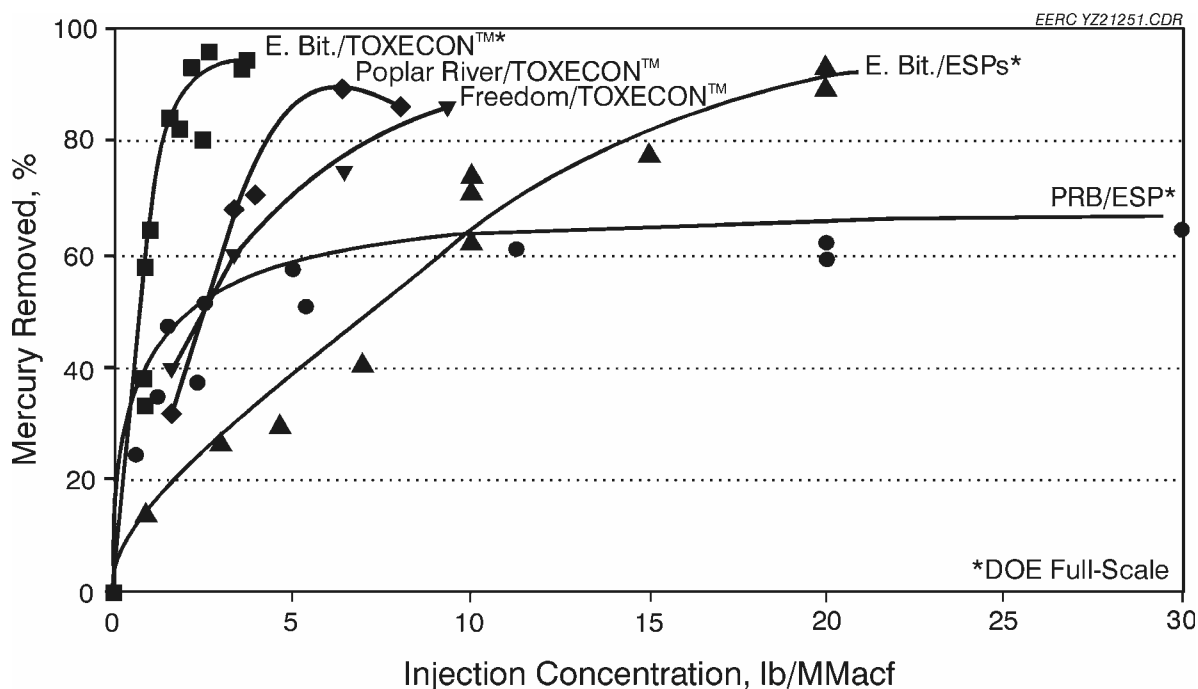
Figure 2. Pilot-scale ESP–FF (8) and full-scale Toxecon™ and ESP (9) Hg removal efficiencies as a function of ACI rate.

Testing conducted at lignite-fired power plants equipped with a spray dryer baghouse (SDA–FF) firing Fort Union lignite indicated poor performance of conventional ACI to control Hg (10). The results indicate control efficiency of less than 35% for DARCO® FGD and lignite-derived activated carbon (LAC). The poor results are due to the low-acid-gas-containing flue gas and the high proportion of Hg^0 in the flue gas stream. The iodine-impregnated activated carbon showed approximately 90% control.

Researchers at the EERC and elsewhere are striving to attain a better understanding of Hg species reactions on activated carbon surfaces in order to produce more efficient sorbents. Functional groups containing inorganic elements such as chlorine or sulfur appear to have a significant role in bonding Hg (11–13). Recently, detailed analysis of sorbents derived from lignites exposed to flue gas and Hg^0 indicated the key species impacting oxidation and retention of Hg on the surface of the carbon contain chlorine and sulfur (14, 15). The chlorine reacts to form organically associated chlorine on the surface, and it appears that the organically associated chlorine on the carbon is the key site responsible for bonding with the Hg^{2+} species.

Amended silicate injection shows promise in controlling Hg emissions at coal-fired power plants (16). The amended silicates have shown improvement factors of 1.5–2 in controlling Hg emissions over activated carbon from subbituminous coal testing in a pilot-scale test. The amended silicates have not been tested using North Dakota lignites.

Mercury Oxidation

Mercury oxidation technologies being investigated for Fort Union lignites include catalysts, chemical agents, and cofiring materials. The catalysts that have been tested include a selective catalytic reduction (SCR) catalyst for NO_x reduction, noble metal-impregnated catalysts, and oxide-impregnated catalysts. The chemical agents include chlorine-containing salts and cofiring fuels that contain oxidizing agents (10).

SCR catalysts were tested for their ability to oxidize Hg; results were mixed. Mercury speciation sampling conducted upstream and downstream of SCR catalysts at power plants that fire bituminous and subbituminous coals (17) showed evidence of mercury oxidation across SCR catalysts when firing bituminous coals. However, when firing subbituminous coals, the results indicate limited oxidation. More testing needs to be conducted on low-rank coals. The ability of the SCR system to contribute to oxidation appears to be coal-specific and is related to the chloride, sulfur, and calcium content of the coal, as well as temperature and specific operation of the SCR catalyst including space velocity.

Mercury oxidation catalysts have shown high potential to oxidize Hg^0. Results in testing a slipstream at a North Dakota power plant indicated over 80% conversion to oxidized mercury for periods of up to 6 months (10). Tests were also conducted using iron oxides and chromium, with little success of oxidation. Galbreath and others (18) have conducted short-term pilot-scale testing with maghemite (γ-Fe_2O_3) additions and were able to transform about 30% of the Hg^0 in North Dakota lignite combustion flue gases to Hg^{2+} and/or Hg(p) and, with an injection of a small amount of HCl (100 ppmv), nearly all of the Hg^0 to Hg^{2+}. Theoretically, the use of chloride compounds to oxidize Hg^0 to Hg^{2+} makes sense. The evidence includes chemical kinetic modeling of bench-scale test results, indicating that the introduction of chloride compounds into the high-temperature furnace region will most likely result in the production of atomic chlorine and/or molecular chlorine, which are generally thought to be the dominant Hg^0 reactants in coal combustion flue gases (4).

Fuel additives for mercury oxidation and sorbent enhancement have recently been tested at the EERC. The results of the addition of materials with coal at very low levels along with the ACI upstream of an ESP–FF, *Advanced Hybrid*™, and ESP only are illustrated in Figure 3. The first part of the figure shows the baseline data for Hg emissions ranging from 9 to 12 $\mu g/Nm^3$, with 80%–90% of the Hg in the elemental form. The second case is ACI followed by the addition of SEA2, showing a reduction in Hg emissions to 90% removal. The third case is the *Advanced Hybrid*™ filter, which produced nearly 90% control efficiency. The final ESP-only case also indicated up to 90% control. The control efficiency for the ESP-only case showed significant potential improvement over past results obtained with the ESP-only illustrated in Figure 1. This technology also has the potential to improve dry FGD baghouse control efficiency.

Sorbent enhancement technologies (also referred to as additives [SEAs]) have also been investigated by ALSTOM Power, Inc. The sorbent preparation system enhances sorbent performance by changing the physical and chemical nature of the sorbent. The enhancement is expected to be applicable to a significant number of sorbents currently utilized for Hg control.
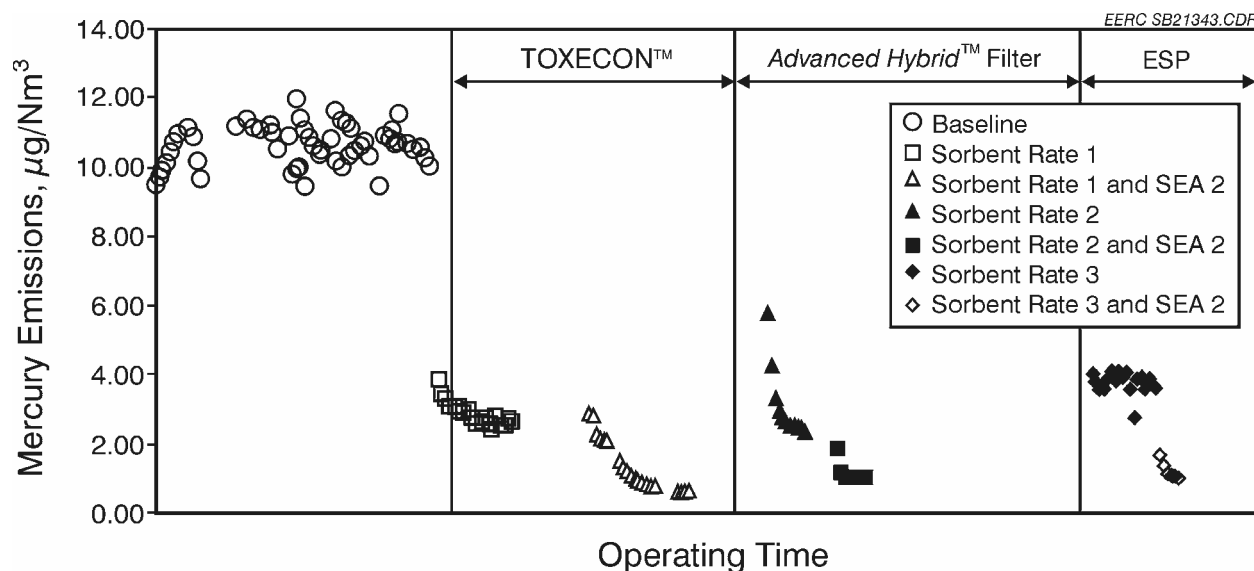
Figure 3. Hg emissions for ACI combined with additives.

The potential for sorbent enhancement has shown an increase from 68% to over 90% capture of Hg. These tests evaluated the performance of baseline and enhanced sorbents in entrained flow. Sorbents were injected in a duct with synthetic flue gas followed by an ESP.

Cofiring TDF at Otter Tail Power Company's Big Stone Plant has been suspected to contribute to the very high reactivity of Hg with fly ash and also with carbon sorbents while firing a low-chlorine PRB coal (19). During periods of operation that coincide with cofiring TDF, enhanced Hg oxidation and removal of Hg by a particulate control device (PCD) have been observed. When about 3%–5% (Btu basis) TDF was cofired with coal at the power plant, measurements showed that the average PCD inlet Hg speciation was 55% particulate bound, 38% oxidized, and 6.4% elemental. Without carbon injection to the PCD, the natural Hg capture efficiency of the PCD was 49%. Furthermore, a carbon injection rate of 24 kg carbon/million m^3 flue gas resulted in a 91% total Hg capture efficiency at the PCD. These field test results indicate that cofiring TDF has the effect of changing the speciation of Hg at the inlet to the PCD, which facilitates Hg collection at the PCD.

Since 1995, DOE has supported development of a new concept in particulate control called the AHPC (19). The AHPC has been licensed to W.L. Gore & Associates, Inc., and is now marketed as the *Advanced Hybrid*™ filter by Gore. The *Advanced Hybrid*™ combines the best features of ESPs and baghouses in a unique configuration, providing major synergism between the two collection methods, both in the particulate collection step and in the transfer of dust to the hopper. The *Advanced Hybrid*™ filter provides ultrahigh collection efficiency, overcoming the problem of excessive fine-particle emissions with conventional ESPs, and it solves the problem of reentrainment and re-collection of dust in conventional baghouses. The *Advanced Hybrid*™ filter appears to have unique advantages for Hg control over baghouses or ESPs as an excellent gas–solid contactor. The *Advanced Hybrid*™ filter technology can be a very cost-effective retrofit technology for plants with existing ESPs.

Introduction

TASK 1 – MERCURY CONTROL ENHANCEMENT FOR UNSCRUBBED SYSTEMS EQUIPPED WITH ESPS

The goal of the tests performed was to evaluate selected furnace additives and flue gas sorbents for mercury removal enhancement in a coal-fired combustion system equipped with an ESP.

Experimental

Pilot-Scale Facility and Test Plan

A 550,000-Btu/hr pc-fired unit, known as the PTC, was used to fire lignites and test mercury control options. The coal combustion flue gas exiting the PTC was cooled down to a nominal temperature of 149°C (300°F) and then introduced into a single-wire tubular ESP unit. Figure 4 shows the schematic diagram of the system. Furnace additives were added to coal prior to introduction to the furnace. Mercury sorbents were fed with a K-Tron dual-screw feeder upstream of the ESP. The feeder was calibrated prior to the start of carbon injection. In addition, the weight of carbon added during a run was divided by the time of injection to provide an average feed rate. According to the calibration data and weight-of-added-carbon data, the feeder appeared to provide a very steady and consistent feed rate within a few percentage points of the target rate. The carbon feed and injection system worked very well, and there were no problems with inconsistent feeding or plugging of the feeder or injection system.

Continuous mercury monitors (CMMs) were used to monitor mercury vapor concentrations at the ESP inlet (Site 1) and outlet (Site 2) 24 hours per day for the entire testing period. Several Ontario Hydro (OH) method samples (American Society for Testing and
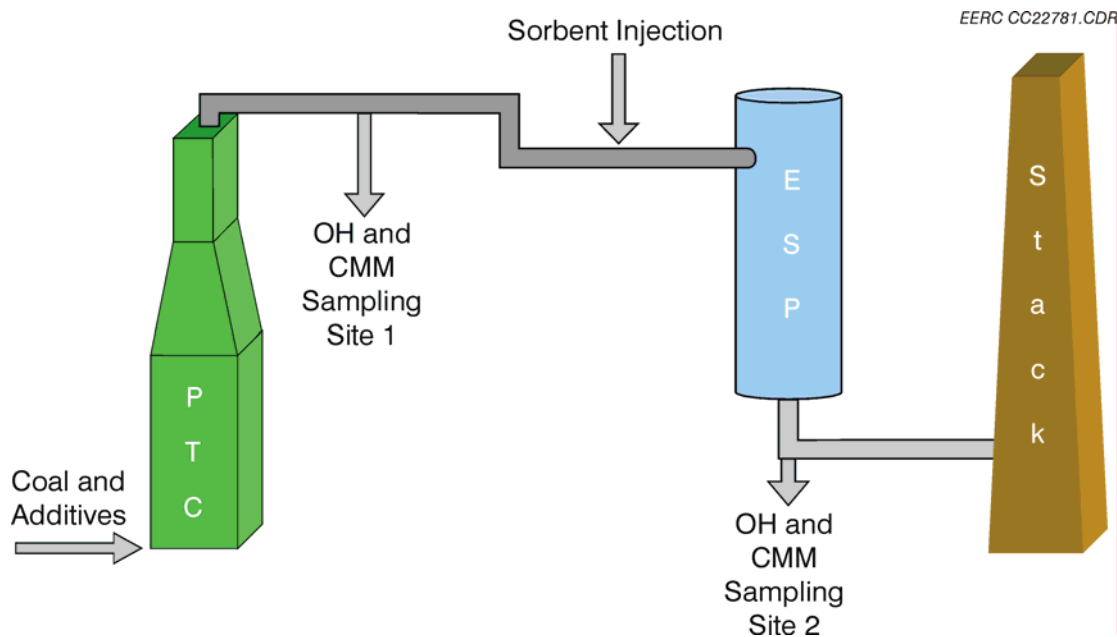
Figure 4. Injection and sampling schematic of the PTC with an ESP.

Materials [ASTM] D6784 Standard Test Method for Elemental, Oxidized, Particle-Bound, and Total Mercury in Flue Gas Generated from Coal-Fired Stationary Sources) were collected at the ESP inlet and outlet throughout the testing period as verification of the CMM data.

The pilot-scale test was started on September 8, 2003, and completed on September 19, 2003. Fourteen tests were completed to evaluate the performance of various sorbent and mercury oxidants on mercury removal across the ESP as a function of feed rate. A detailed test matrix is listed in Table 1. Ten additional tests were performed to evaluate mercury control with the *Advanced Hybrid*™ filter and are summarized in the Results and Discussion section of Task 4.

Coal and Combustion Flue Gas Analyses

North Dakota Freedom lignite was tested in the PTC at the EERC. The proximate and ultimate analysis data for the Freedom lignite are reported in Table 2, showing a concentration of mercury in the range of 0.0503–0.0515 μg/g (dry basis), with a mean value of 0.0508 μg/g. Based on the proximate and ultimate analysis data, it was calculated that 1 lb of coal would produce 89 scf of dry flue gas normalized to a 3.0% oxygen level. From the mercury content in raw coal, the total mercury concentration in flue gas was expected to be 7.2 μg/m³ of dry flue gas (at a 3% oxygen level).

The flue gas compositions, O_2, CO_2, CO, NO_x, and SO_2, at the combustor outlet were monitored during the entire testing period, and hourly average values were calculated and plotted as a function of operating time as shown in Figure 5. The CO concentration was in the range of

Table 1. Test Matrix for Unscrubbed Systems Equipped with ESPs

| Test No. | Mercury Oxidant Additive | | Sorbent | |
	Category	Injection Rate, lb/Macf	Category	Injection Rate, lb/Macf
T1-1(baseline)	None	NA[1]	None	NA
T1-2	None	NA	DARCO® FGD	2.75–18.4
T1-3	NaCl	3.76–14.7	None	NA
T1-4	NaCl	3.76–14.7	DARCO® FGD	2.75–4.59
T1-5	SEA2	1.84–7.34	None	NA
T1-6	SEA2	1.84	DARCO® FGD	2.57
T1-7	NaCl	7.34–11.0	HCl-treated FGD	2.57–4.59
T1-8	None	NA	EERC-treated carbon	1.84–2.75
T1-9	SEA2	1.84	EERC-treated carbon	2.75
T1-10	Zn	7.34	None	NA
T1-11	Zn and NaCl	7.34–11.0	None	NA
T1-12	None	NA	Na_2S_4 (solution)	0.89–6.67
T1-13	$CaCl_2$	11	DARCO® FGD	0–4.59
T1-14	None	NA	ALSTOM sorbent	1.1–3.1

[1] Not applicable.

Table 2. Coal Analysis of Freedom Lignite for Run PTC-FM-639

Proximate Analysis, wt%	As Sampled	Moisture Free
Moisture Content	31.90	NA
Volatile Matter	30.70	45.05
Fixed Carbon	29.12	42.79
Ash	8.29	12.16
Ultimate Analysis, wt%		
Hydrogen	6.33	4.10
Carbon	41.26	60.55
Nitrogen	0.78	1.15
Sulfur	0.73	1.07
Oxygen	42.61	20.97
Ash	8.29	12.16
Mercury Concentration in Coal, µg/g		
Sample 1		0.0503
Sample 2		0.0507
Sample 3		0.0515
Sample 4		0.0505
Mean		0.0508
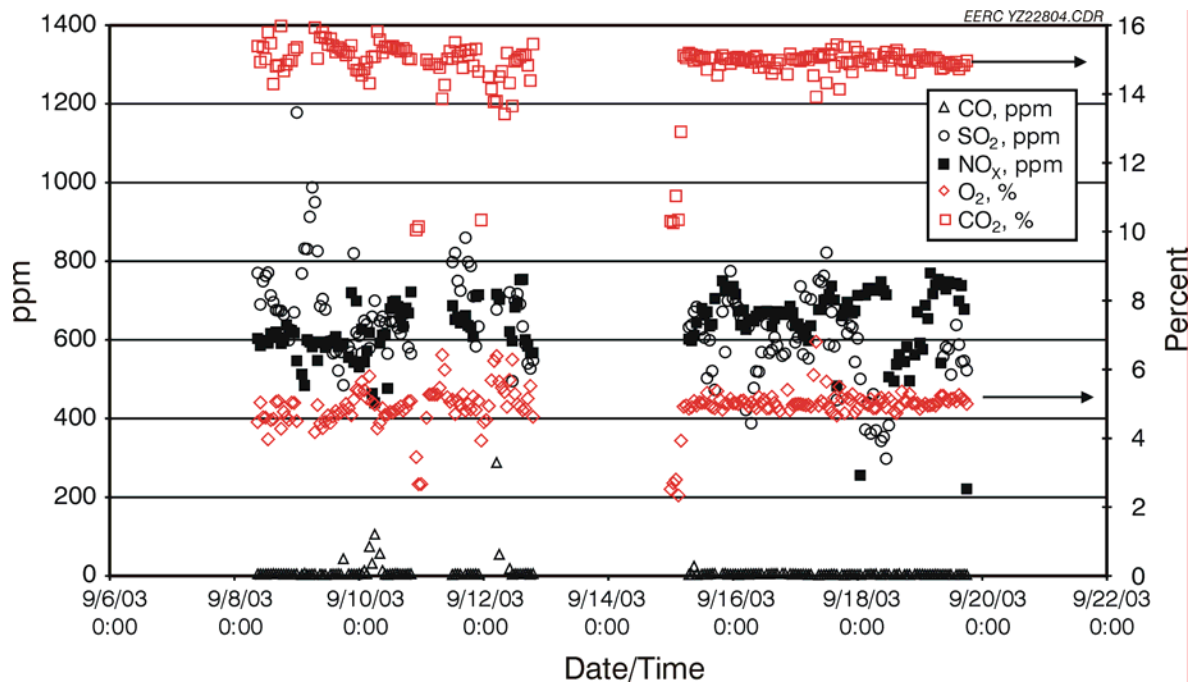
Figure 5. Flue gas compositions in Freedom lignite combustion.

3–6 ppm for most of the testing period, indicating complete coal combustion. CO spikes were observed on September 10–12, 2003, showing somewhat incomplete coal combustion at that time. The SO_2 concentration in the flue gas ranged from 300 to 1200 ppm, depending on the coal

feed rate, while the theoretical value of the SO_2 concentration was calculated at 1026 ppm, based on sulfur content and proximate and ultimate coal analyses. The NO_x concentration in the flue gas was 221–770 ppm. The HCl concentration in flue gas was also measured using EPA Method 26A (Detemination of Hydrogen Halide and Halogen Emissions from Stationary Sources Isokinetic Method), showing 0.58–1.45 ppm. Because of the low levels of CO, NO_x, SO_2, and HCl and historical data, most mercury in the Freedom lignite flue gas was expected to be in the elemental vapor phase (Hg^0).

Mercury Speciation Across the ESP in the Baseline Test

Test T1-1 (Baseline). During the pilot-scale test, Freedom lignite with a mean mercury content of 0.05 μg/g (dry basis) was combusted at a nominal feed rate of 87 lb/hr. The coal combustion flue gas exiting the PTC was cooled down to a nominal temperature of 149°C (300°F) and then introduced into a single-wire tubular ESP unit. The ESP was operated at 40–60 kV, with a corona current of 4.0 mA. The collection plates and electrodes were rapped every 120 min. The hopper ash was emptied between tests. Two CMMs were used to monitor mercury vapor concentrations at the ESP inlet and outlet. OH method samples were collected to verify the CMM data. The purpose of the baseline test (T1-1) was to establish speciated mercury concentrations in Freedom lignite flue gas and determine whether there was a change in speciation across the ESP unit. Based on CMM data, the daily average mercury vapor concentrations in Freedom lignite combustion flue gas, both total and speciated, are shown in Figure 6. The error bars represent plus or minus one standard deviation. No particulate mercury for the CMM is shown because the flue gas was sampled through a filter. Oxidized
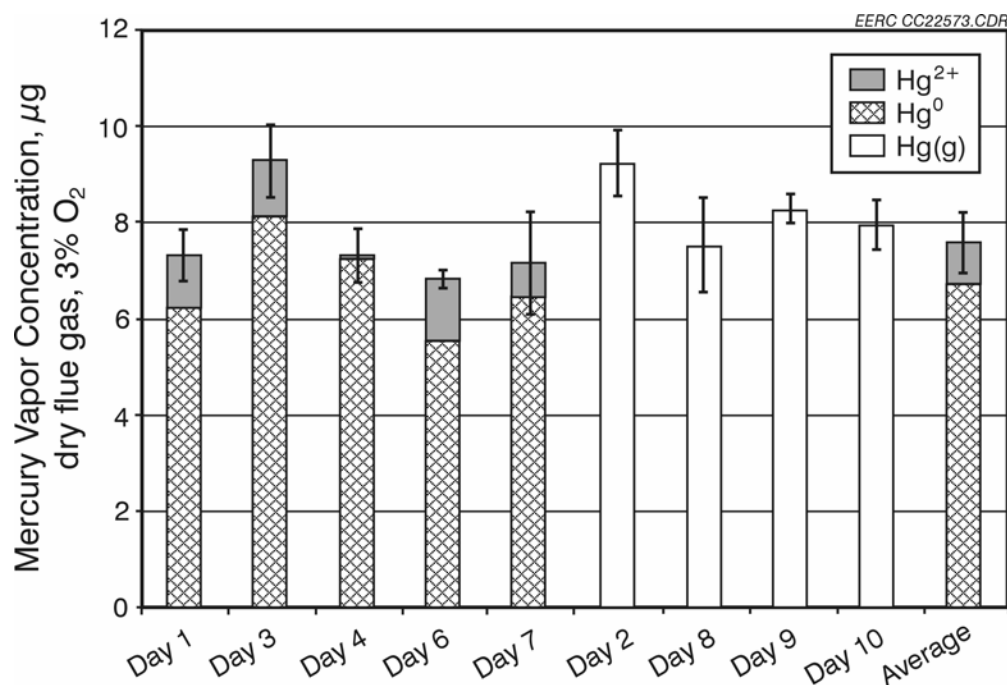
Figure 6. Mercury vapor concentration in Freedom coal flue gas – baseline.

mercury vapor in the flue gas was in the range of 0.09–1.30 $\mu g/Nm^3$, while elemental mercury (Hg^0) vapor was in the range of 5.52–8.13 $\mu g/Nm^3$. The total mercury vapor concentration (Hg[g]) in the flue gas varied from 6.8 to 9.2 $\mu g/Nm^3$ (dry flue gas, 3% O_2), showing an average mercury level of 7.57 $\mu g/Nm^3$, compared to the theoretical value of 7.2 $\mu g/Nm^3$ obtained from the coal combustion calculation based on the coal analysis. The above CMM data indicate that most of the mercury released from Freedom lignite combustion was in the vapor phase before it entered the ESP and elemental mercury vapor was the dominant species.

To determine inherent mercury capture by fly ash across the ESP, mercury concentrations were measured with CMMs and the OH method both at the ESP inlet and outlet, and the results are plotted in Figure 7. Both methods indicate that the majority of mercury was present as elemental mercury vapor, with a small fraction (10.9%–12.9%) of oxidized mercury and nearly no particulate-associated mercury at the ESP inlet. The total mercury concentration at the ESP outlet was almost the same as the ESP inlet, showing virtually no mercury capture across the ESP because of the low level of particulate mercury in the flue gas, which is very typical for North Dakota lignite with the ESP configuration. A comparison between the two sampling methods shows consistent results, with the OH method measurement slightly higher than the CMM results. ESP hopper ash was collected to analyze mercury content, loss on ignition (LOI), and chlorine and sodium concentrations. The results are listed in Table 3. The mercury content in the ESP hopper ash was 0.0139 $\mu g/g$, close to the 0.003–0.00783 $\mu g/g$ at the ESP inlet, as indicated by the OH method data. This was not surprising based on the low levels of LOI (0.35%) and chlorine (206 $\mu g/g$) in the ESP hopper ash.
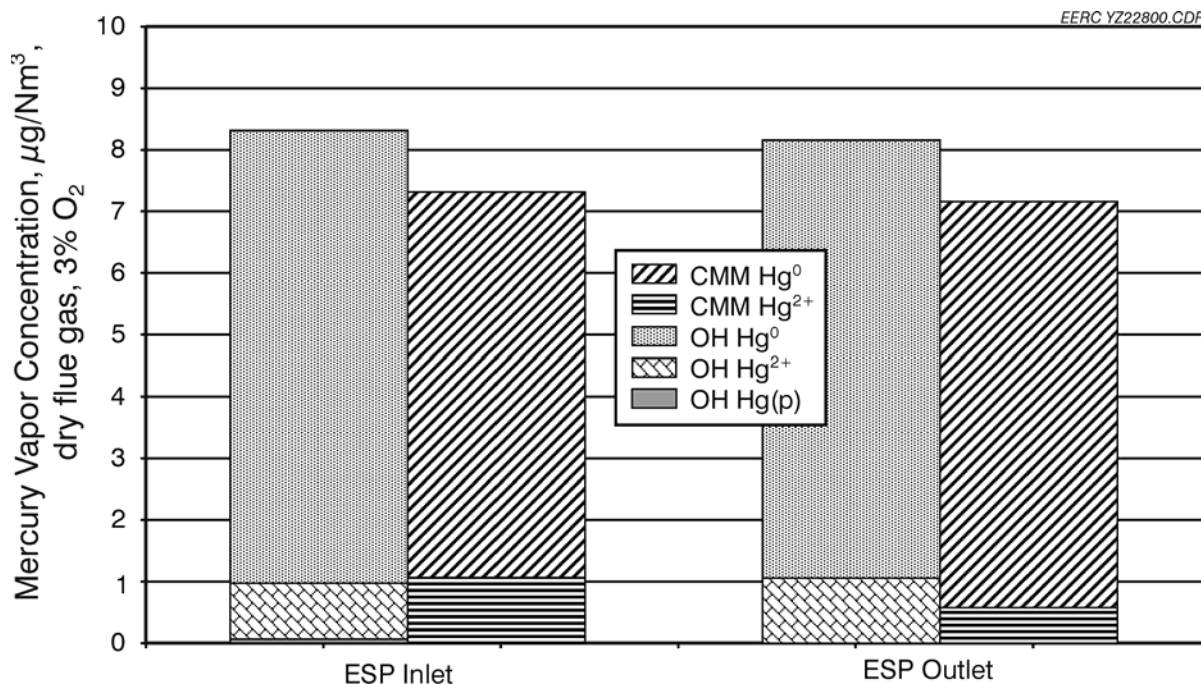
Figure 7. Mercury speciation across the ESP baseline data for Freedom coal, 300°F.

Table 3. ESP Hopper Ash Analysis Results – NaCl–FGD Injection

	Baseline	DARCO® FGD	NaCl	NaCl + DARCO® FGD
LOI, %	0.35	1.28	0.46	0.94
Mercury, µg/g	0.0139	0.189	0.198	0.381
Chlorine, µg/g	206	NA	3820	5440
Sodium, µg/g	11,200	NA	12,200	18,700

Mercury removal across the ESP was evaluated with sorbent injection, mercury oxidant addition, and a combination of sorbent and mercury oxidant. The sorbents were injected upstream of the ESP, while the mercury oxidants were added to the coal prior to introduction to the furnace. As listed in Table 1, the sorbents included DARCO® FGD activated carbon, EERC-pretreated activated carbon, and ALSTOM sorbent technology. Mercury oxidants included NaCl, $CaCl_2$, Zn, and SEA2.

Results and Discussion

Mercury Control Technology Results

Tests T1-2 to T1-4. Two tests were performed to evaluate DARCO® FGD carbon, mercury oxidant NaCl, and their combination on mercury removal in Freedom flue gas across the ESP. DARCO® FGD carbon was injected upstream of the ESP at varied feed rates from 4.59 to 18.4 lb/Macf. Figure 8 shows the temporal variation in total mercury vapor concentration
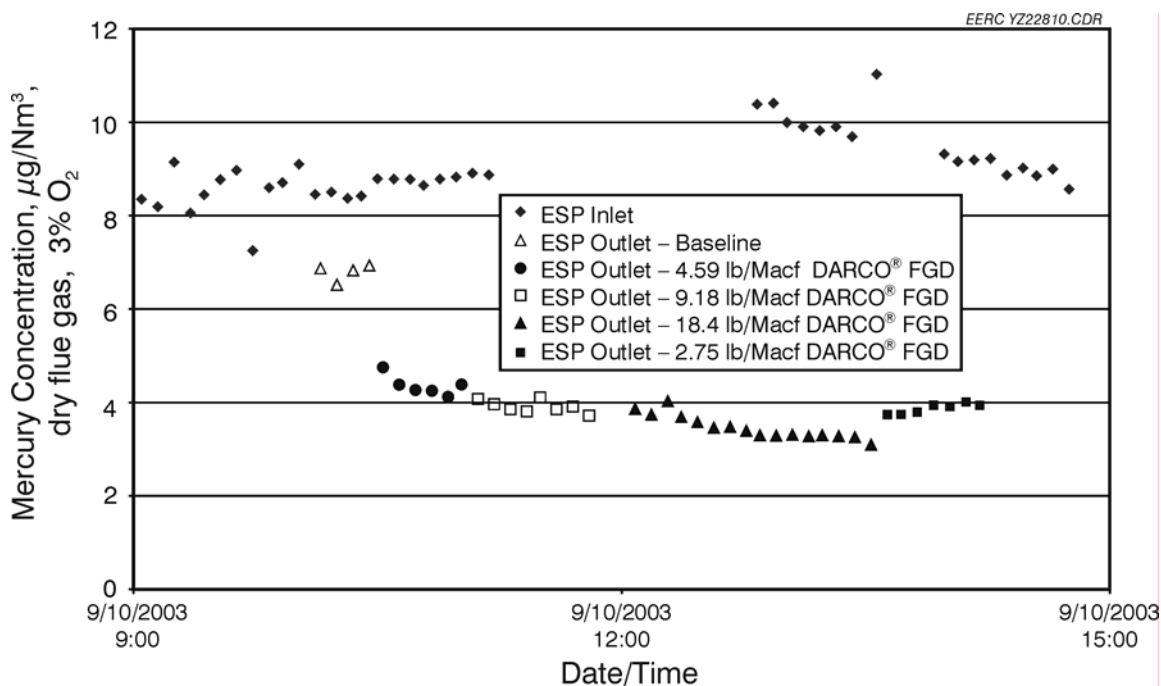
Figure 8. Mercury vapor concentrations at the ESP inlet and outlet during DARCO® FGD carbon injection (Freedom coal, 300°F).

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(measured by CMM) downstream from the ESP while the total mercury vapor concentration at the ESP inlet was in a relatively stable range of 8–10 $\mu g/Nm^3$. Mercury removal efficiencies across the ESP were calculated based on the CMM data at the ESP inlet and outlet and are plotted as a function of injection rate in Figure 9. The mercury removal was 51.5% at 4.59 lb/Macf, increased to 59% at 9.18 lb/Macf, and reached 67.2% at 18.4 lb/Macf sorbent injection. The OH mercury speciation data were collected at the 18.4-lb/Macf injection test (Figure 10), showing DARCO® FGD carbon-only captured 60% of the total mercury in flue gas. Since there are low levels of particulate-associated mercury in flue gas, the total mercury collection efficiency calculated based on the OH data is similar to the CMM results (also shown in Figure 9). During DARCO® FGD carbon injection, the LOI level in the ESP hopper ash increased to 1.28% and the mercury concentration was 0.189 $\mu g/g$, higher than the 0.0139 $\mu g/g$ in baseline test (also listed in Table 3).

The above results indicate that large amounts of DARCO® FGD carbon are required for efficient mercury removal across the ESP for Freedom lignite flue gas due to the low reactivity and the mass transfer limit between gaseous mercury and the in-flight DARCO® FGD carbon.

Previous research at the EERC indicated that cofiring NaCl and coal can enhance mercury reactivity with sorbents and mercury oxidation in flue gas. Herein, solid NaCl was fed into the furnace with Freedom lignite to investigate its impact on mercury emissions out of the ESP systematically. NaCl feed rate varied from 3.6 to 14.7 lb/Macf, corresponding to 1.1–4.23 lb-NaCl/ton-coal. Mercury removal efficiency across the ESP by NaCl addition alone is also plotted in Figure 9, showing NaCl significantly improved mercury capture by changing mercury
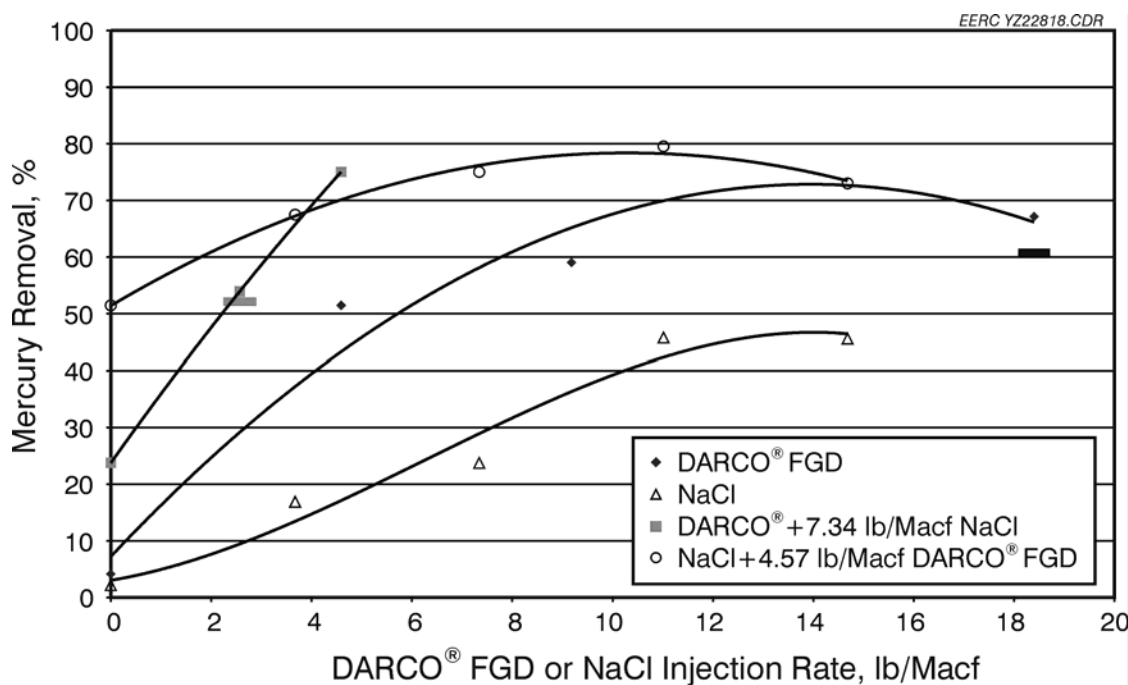
Figure 9. Effect of NaCl and DARCO® FGD performance for mercury control in ESP.
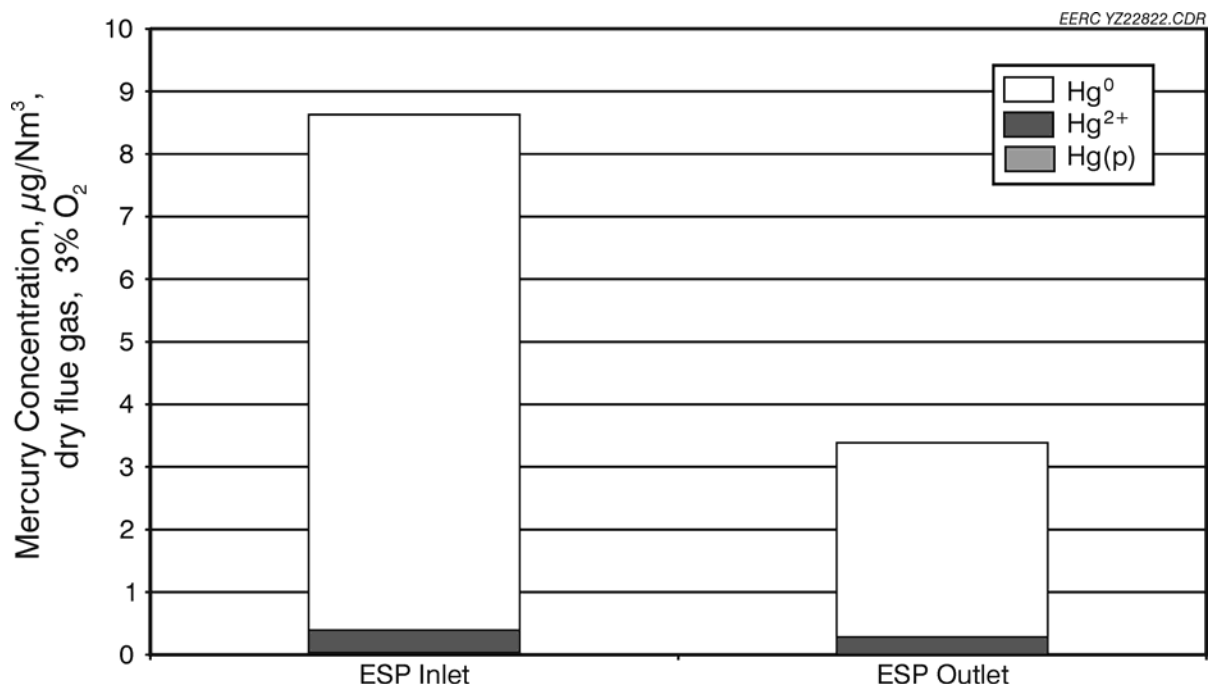
Figure 10. OH speciation across ESP with 18.4 lb/Macf DARCO® FGD injection (Freedom, 300°F).

chemistry in flue gas. Mercury removal increased proportionately with increased NaCl additive, from virtually no inherent mercury capture to 45.6% at 14.7 lb/Macf NaCl addition. Since both the mercury and chlorine concentrations in the ESP hopper ash were dramatically enriched while sodium and LOI concentrations were similar to the baseline test (Table 3), it is hypothesized that atomic chlorine released from NaCl decomposition in the combustion zone enhances mercury oxidation and capture on fly ash. More research is needed to further understand the detailed chemistry mechanisms.

Test T1-4 was performed to evaluate the integrated impact on mercury removal across the ESP while both NaCl and DARCO® FGD carbon were utilized. Figure 11 shows temporal variations in gaseous mercury concentration at the ESP inlet and outlet measured by CMMs. The mercury ESP outlet concentration was reduced from ~6.5 $\mu g/Nm^3$ at the baseline test to 2.4 $\mu g/Nm^3$ when 3.67 lb/Macf of NaCl was fed into the furnace and 4.59 lb/Macf DARCO® FGD carbon was injected upstream of the ESP. With an increased NaCl feed rate of 11 lb/Macf, the mercury emissions reduced to 1.56 $\mu g/Nm^3$, and elemental mercury was the dominant species. It is also noted that the fly ash generated with NaCl addition caused biased CMM measurement at the ESP inlet because the fly ash filter cake formed upstream of the CMM unit adsorbed a portion of the mercury vapor. Therefore, the baseline mercury data at the ESP inlet are used for mercury removal calculations. The mercury collection efficiencies under a constant DARCO® FGD carbon injection (4.59 lb/Macf) and varied NaCl addition rates (0–14.7 lb/Macf) are plotted in Figure 9 for comparison. The 4.59-lb/Macf DARCO® FGD carbon injection had a 51.5% mercury removal. When 3.67 lb/Macf NaCl was added, the overall mercury collection efficiency increased to 67.5%, an additive response from DARCO® FGD carbon (51.5% at
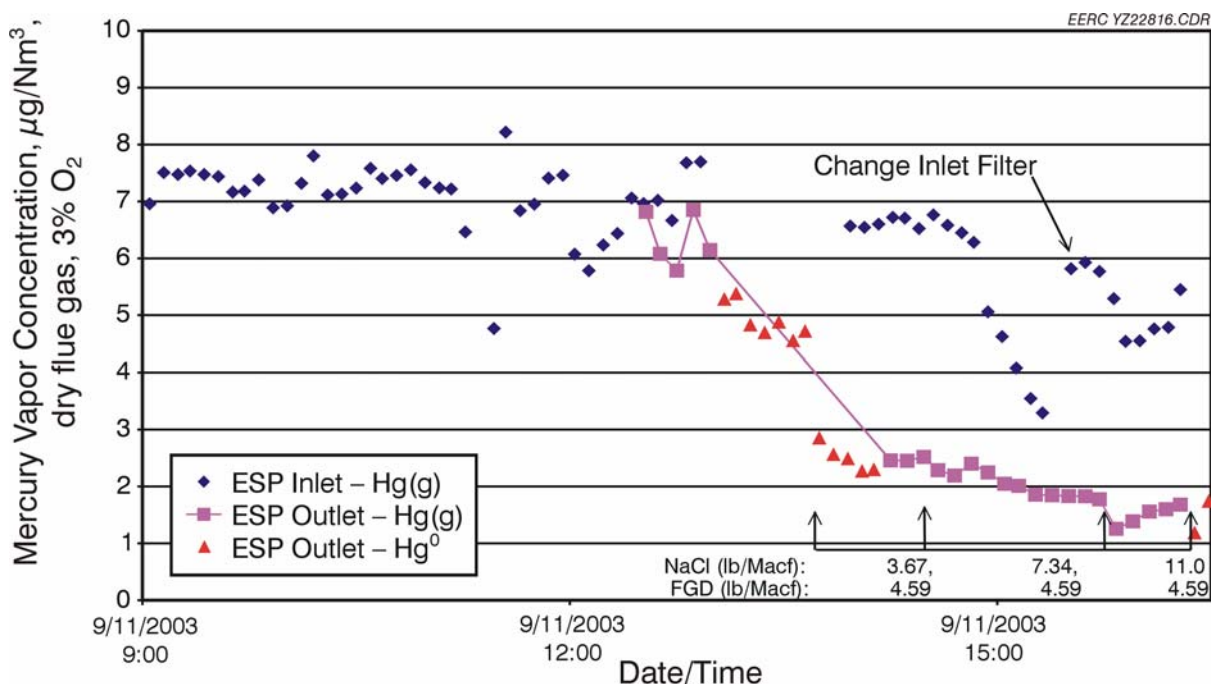
Figure 11. Mercury vapor concentrations at the ESP inlet and outlet during DARCO® FGD–NaCl injection (Freedom coal, 300°F).

4.59 lb/Macf injection alone) and NaCl (an additional 16.9% at 3.67 lb/Macf injection). The additive effect was also shown at the test of 7.34 lb/Macf NaCl (an increase of 23.7%) and 4.59 lb/Macf DARCO® FGD carbon (51.5%) with an overall mercury removal of 75%. With further increasing NaCl feed rate, however, the overall mercury removal only increased marginally to approximate 80%, indicating it may become mass transfer-limited.

Another short-term test was conducted to further confirm the additive effect of the DARCO® FGD–NaCl combination with a constant 7.34 lb/Macf NaCl and varied 0–4.59 lb/Macf DARCO® FGD carbon injection. The overall mercury removal (Figure 9) was from 23.7% at 7.34 lb/Macf NaCl injection alone to 75% at 7.34 lb/Macf NaCl plus 4.59 lb/Macf DARCO® FGD carbon injection, indicating the additive effect from DARCO® FGD–NaCl.

A 22-h test was carried out during September 17–18, 2003, to obtain long-term results on the performance of NaCl–DARCO® FGD carbon on mercury removal across the ESP. 2.57 lb/Macf DARCO® FGD carbon was injected into the ESP, and 7.34 lb/Macf NaCl was fed into the furnace. The mercury emission plotted as a function of operating time in Figure 12 shows a stable value of ~3.6 μg/Nm³ during the testing period. Mercury speciation data collected with the OH method (shown in Figure 13) indicate both elemental and oxidized mercury were depleted across the ESP, having an overall mercury removal of 52.1%, which agrees with the CMM measurement result (Figure 9).

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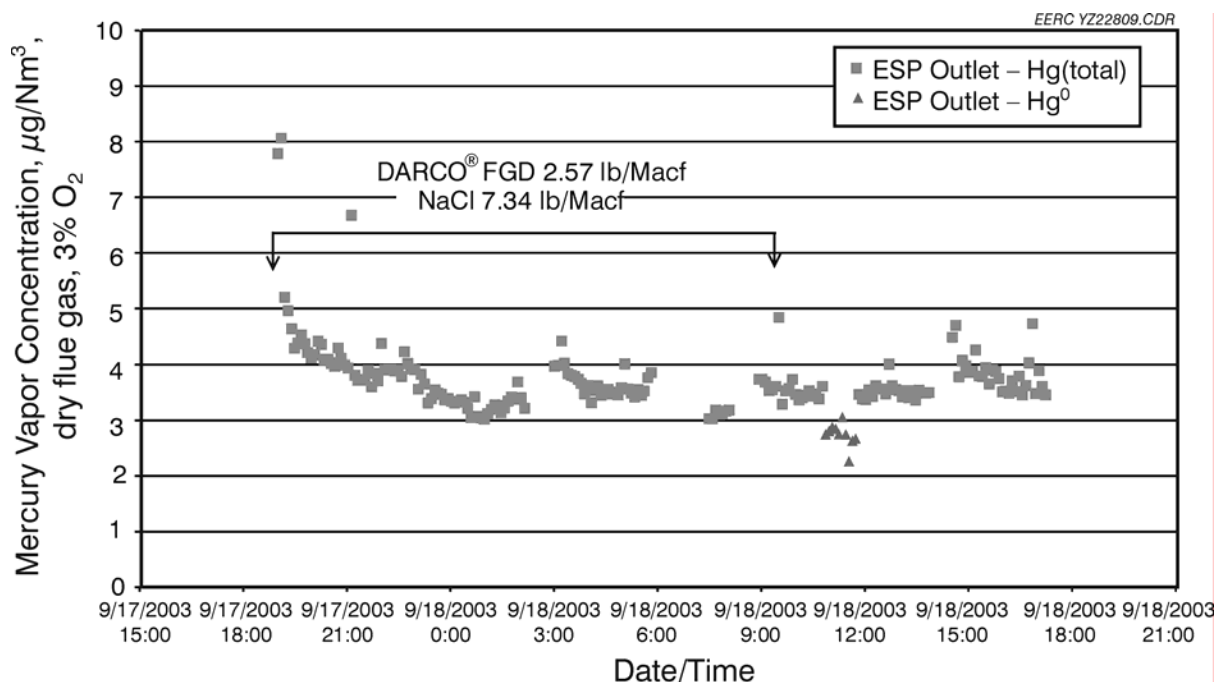
Figure 12. Mercury vapor concentrations at the ESP outlet during DARCO® FGD–NaCl injection long-term test (Freedom coal, 300°F).
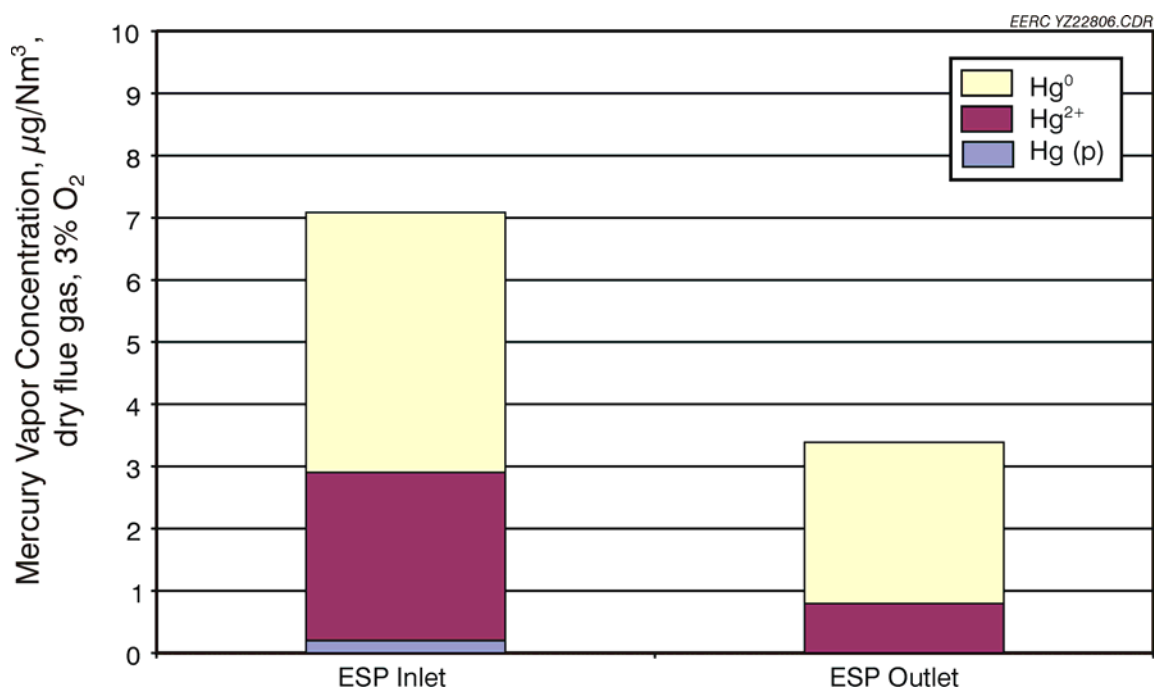
Figure 13. Mercury speciation across ESP with NaCl–DARCO® FGD carbon injection (Freedom coal, 300°F).

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Tests T1-5 and T1-6. Another mercury oxidant tested was SEA2. Limited short-term tests were performed to evaluate its impact on mercury emissions across the ESP as a function of injection rate (Figure 14). SEA2 addition to the furnace significantly enhanced mercury removal, reaching 63.5% at 7.34 lb/Macf SEA2 injection, compared to the approximately 8% inherent fly ash capture without SEA2 addition. The efficiency curve for NaCl addition is also plotted in Figure 14 as a comparison, showing that SEA2 was almost three time as effective as NaCl. ESP hopper ash was collected during the SEA2 addition test for mercury, LOI, SEA2, and sodium analyses. The analysis results (Table 4) showed a strong correlation between mercury and SEA2 in ash, which indicates that SEA2 species in high-temperature flue gas effectively convert gaseous mercury to particulate-associated mercury. Introduction of SEA2 at 1.84 lb/Macf in combination with 2.57 lb/Macf DARCO® FGD improved mercury removal dramatically from 25% (at 2.57 lb/Macf DARCO® FGD injection) to 76.1%. The significant improvement by DARCO® FGD–SEA2 is not merely an additive effect but more a synergistic response. The SEA2 addition in the combustion zone not only enhances gaseous mercury conversion to particulate-associated mercury, but also improves DARCO® FGD carbon reactivity with mercury species.
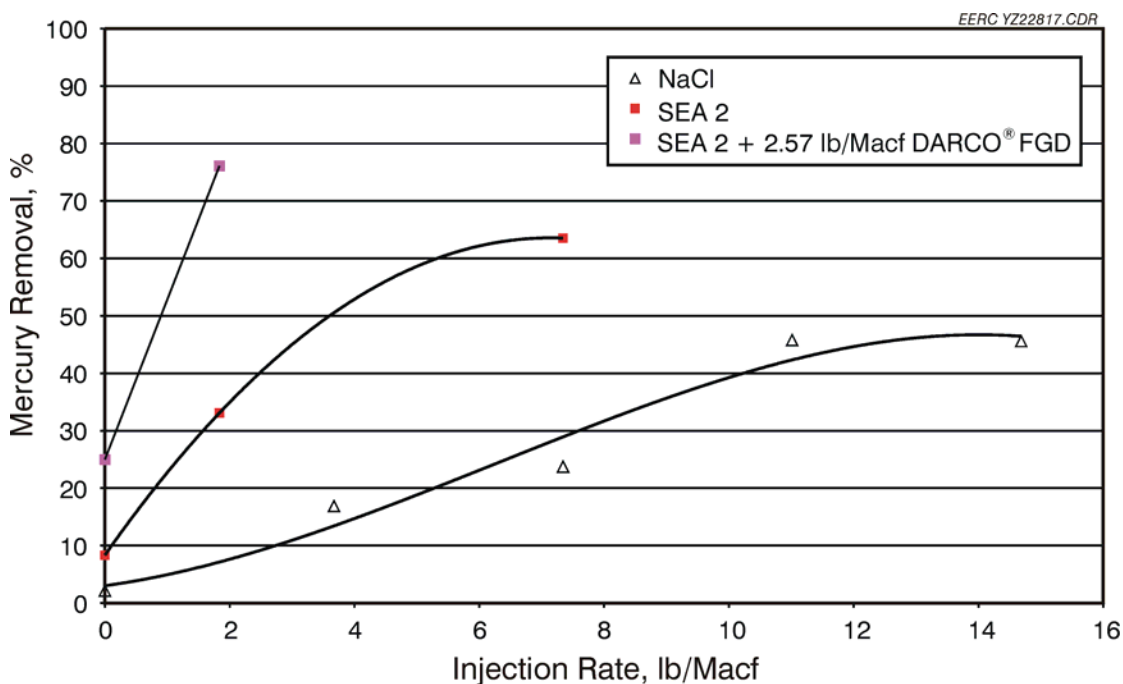
Figure 14. Effect of SEA2 and DARCO® FGD on mercury control in the ESP.

Table 4. ESP Hopper Ash Analysis Results – SEA2 Injection

	Mercury, µg/g	LOI, %	SEA2, µg/g	Sodium, µg/g
Baseline	0.0139	0.35	<30	11,200
SEA2 Injection	0.203	0.46	12,600	18,600

Tests T1-7 to T1-9. The above tests have indicated that the mercury oxidants NaCl and SEA2 benefit mercury removal by enhancing mercury reactivity with fly ash and DARCO® FGD. Therefore, the EERC developed two sorbents, an HCl-treated carbon and an EERC-treated carbon, that were tested to evaluate their effectiveness on mercury removal across the ESP. The two sorbents were injected upstream of the ESP, and the CMM data for each are plotted as a function of operating time (Figures 15 and 16). The ESP outlet mercury concentration was 7 μg/Nm^3 in the baseline test while the mercury concentration at the ESP inlet was around 8–9 μg/Nm^3 (Figure 15). With the 1.84-lb/Macf EERC-treated carbon injection rate, mercury emissions at the ESP outlet decreased to 2.4 μg/Nm^3 and further decreased to 1.74 μg/Nm^3 at the 2.75-lb/Macf EERC-treated carbon injection rate. At the end of the EERC-treated carbon injection test, 1.84 lb/Macf SEA2 was added to the coal feed to enhance mercury removal, with a marginal decrease in mercury to 1.4 μg/Nm^3 at the ESP outlet. Mercury emissions with HCl-treated carbon in combination with NaCl addition are plotted in Figure 16. Mercury removal efficiencies are calculated and plotted as a function of injection rate in Figure 17. Both pretreated sorbents show much better performance for mercury capture than the DARCO® FGD carbon. At the rate of 2.75 lb/Macf EERC-treated sorbent injection, the overall mercury removal was 76.8%, which increased to 82% when 1.84 lb/Macf SEA2 was fed into the furnace. With the combination of NaCl- and HCl-treated sorbent injection, the mercury collection efficiency increased from 23.7% (mercury capture at the 7.34 lb/Macf NaCl injection rate) to 85.1% at 4.59 lb/Macf HCl-treated sorbent plus 7.34 lb/Macf NaCl injection. This collection efficiency was further increased to 90.5% when the NaCl injection rate increased to 11 lb/Macf.
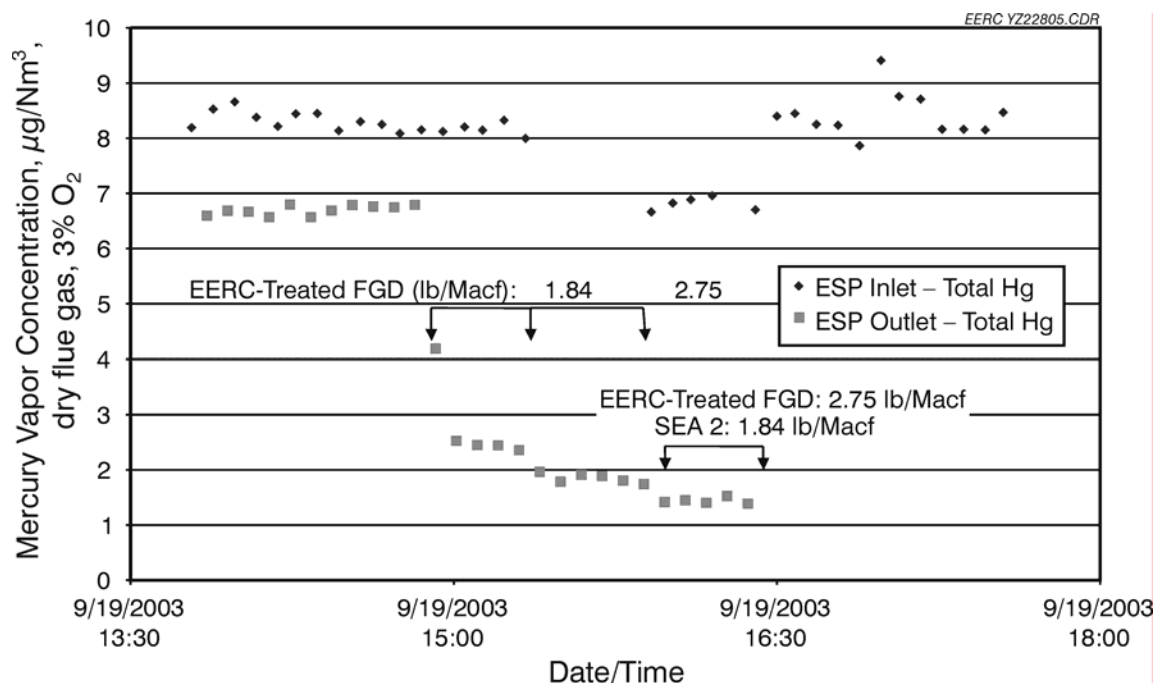
Figure 15. Mercury vapor concentrations at the ESP inlet and outlet during EERC-treated FGD carbon injection (Freedom coal, 300°F).

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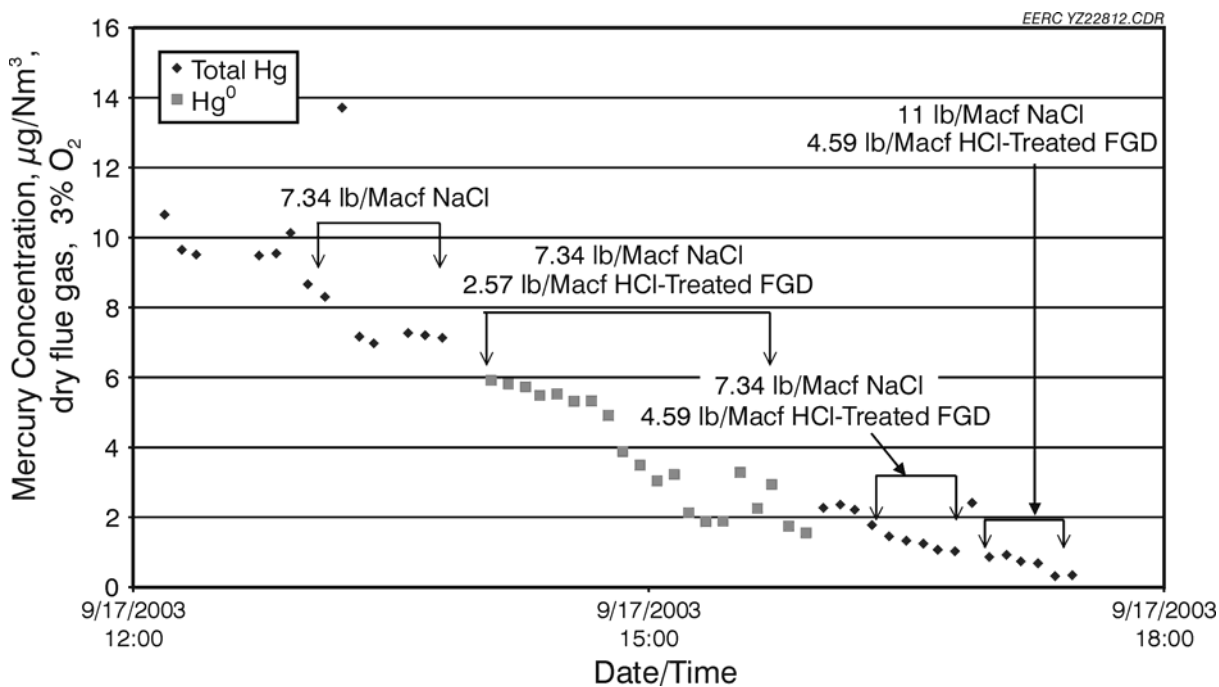
Figure 16. Mercury vapor concentration at the ESP outlet during HCl-treated FGD–NaCl injection.
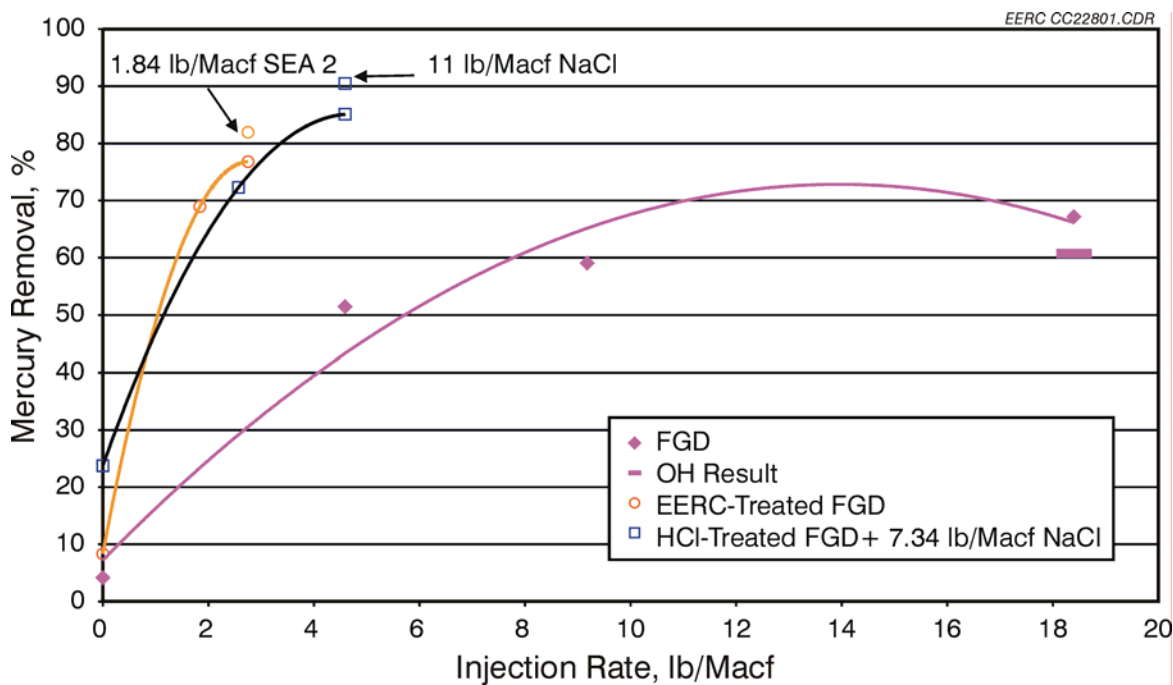
Figure 17. Mercury capture in the ESP with different sorbent injection (Freedom coal, 300°F).

T1-10 to T1-13. Short-term tests were carried out to examine the effects of other potential sorbents and oxidants on mercury removal across the ESP. Sodium tetrasulfide (Na_2S_4) solution was sprayed into the 300°F flue gas before it entered the ESP. Metallic zinc powder and $CaCl_2$ (aq) were added into the furnace separately. The corresponding mercury collection efficiencies are calculated based on the CMM data (Figure 18). With 11 lb/Macf $CaCl_2$ addition, the mercury removal was 44%, the same as the 11-lb/Macf NaCl injection result. Both NaCl and $CaCl_2$ injection outperformed the Na_2S_4 and NaCl plus zinc additions. Zinc addition alone was completely ineffective at mercury capture in the ESP. Also, metallic zinc has a negative impact on NaCl to prohibit mercury capture, probably as a result of competing reactions with the chlorine species. The combination of $CaCl_2$ and DARCO® FGD improved mercury removal from 44% to 73%.

Test T1-14. ALSTOM has developed several mercury sorbent enhancement technologies that were tested in the pilot-scale experiments. The mercury removal efficiencies of ALSTOM sorbents are plotted versus injections as shown in Figure 19. All four sorbents performed much better than the reference DARCO® FGD carbon. At a nominal 1.2-lb/Macf injection rate, the mercury removals ranged from 53% to 86%. Results of OH sampling correlated well with the CMM measurement. Because of the confidential nature of ALSTOM's sorbent technology, more detail of the technology was not provided to the EERC. ALSTOM is preparing information that can be shared with the consortium related to system costs and any balance-of-plant impacts.
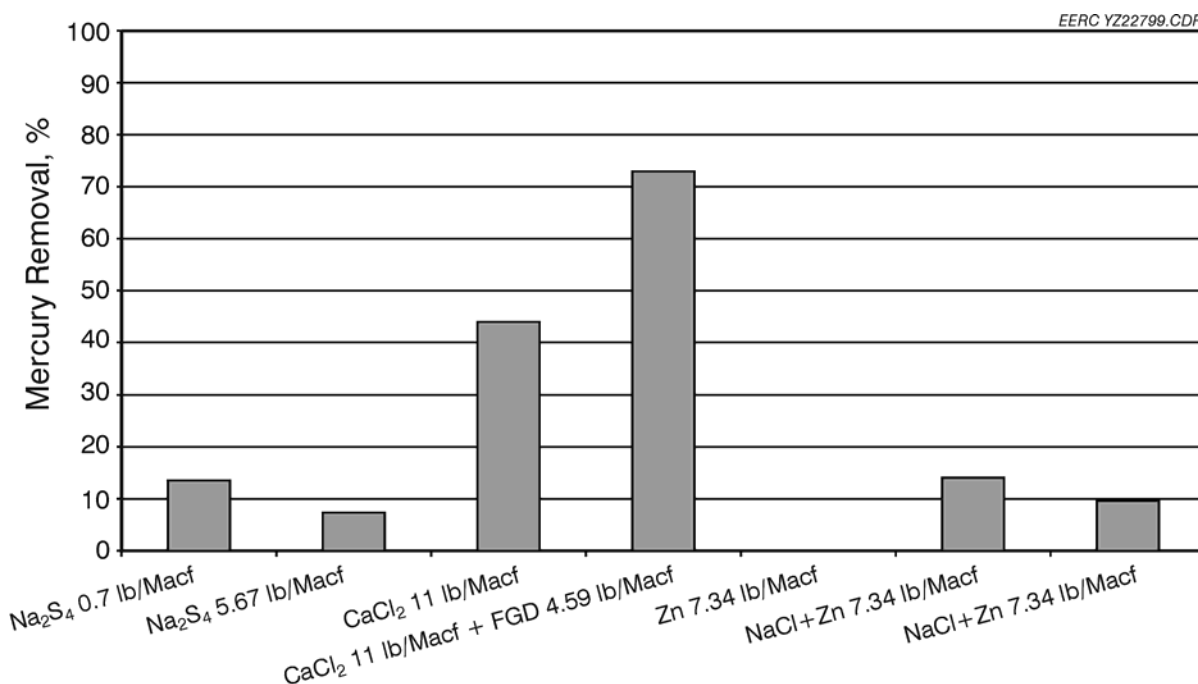
Figure 18. Effects of other additives on mercury capture in an ESP (Freedom coal, 300°F).
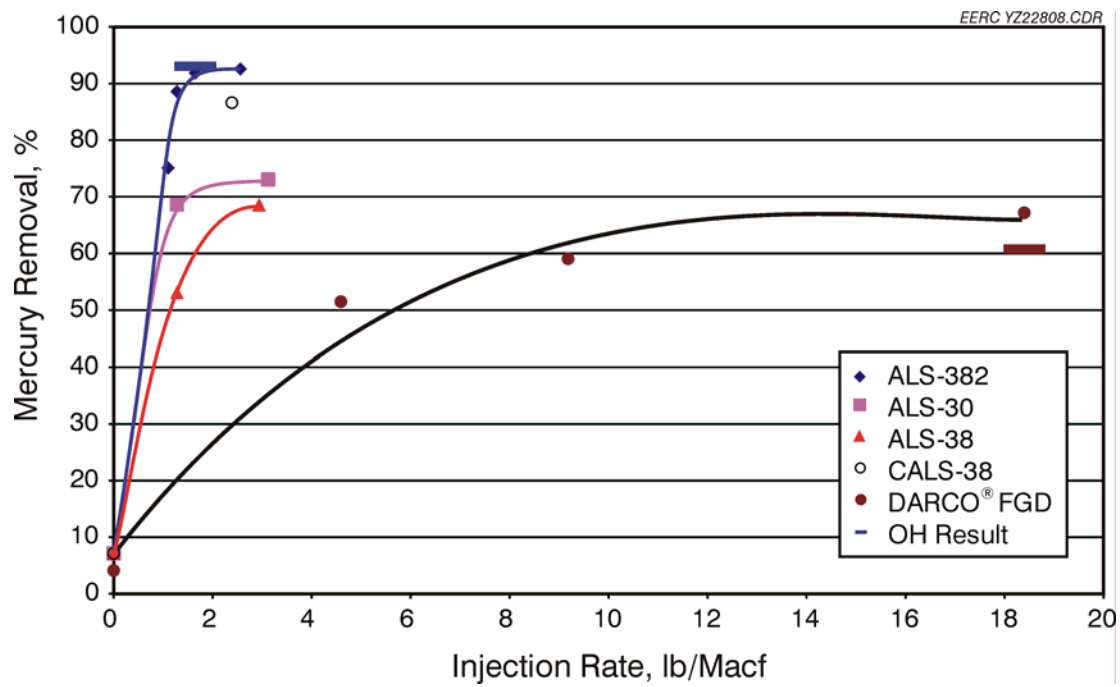
Figure 19. Mercury removal in an ESP with ALSTOM sorbent injection technologies (Freedom coal, 300°F).

TASK 2 – MERCURY OXIDATION UPSTREAM OF DRY SCRUBBERS

The effectiveness of three potential Hg sorbents (DARCO® FGD, Amended Silicate™, and EERC-treated FGD) and three Hg^0 oxidation and sorbent enhancement additives (NaCl, CaCl$_2$, and SEA2) to enhance the Hg removal efficiency of a SDA–FF pollution control system was evaluated using a pilot-scale pc-fired unit. The sorbents and additives were selected based on previous pilot-scale testing of ESP Hg removal effectiveness. A Center lignite coal was combusted in the unit at approximately 580 MJ/hr (550,000 Btu/hr) while Hg concentrations were almost continuously monitored at the SDA inlet and FF outlet to evaluate Hg removal performance. The Hg sorbents and Hg^0 oxidation and sorbent enhancement additives were evaluated separately, and all except the Amended Silicate™ and EERC-treated FGD were also tested in combination. The testing occurred during a 4-day period, December 8–11, 2003.

Experimental

Mercury Sorbent Descriptions

NORIT Americas Inc. DARCO® FGD. DARCO® FGD is a LAC manufactured specifically for the removal of heavy metals and other pollutants typically found in incinerator flue gas streams. It has been proven in numerous incinerator facilities to be highly effective for removing gaseous Hg, dioxins, and furans. Bench-scale tests indicate a Hg^0 sorption capacity of about 100 µg/g (12). Testing in pilot-scale combustion systems indicates that the effectiveness of DARCO® FGD to remove Hg from coal combustion flue gases is variable depending on the flue gas composition, residence time, PCD, and temperature (13, 20, 21). General properties and characteristics of DARCO® FGD, as advertised by NORIT Americas Inc., are presented in Table 5. Duplicate Malvern particle-size analyses of the DARCO® FGD indicated volume median diameters of 16.2 and 18.1 µm. The chemical composition of inorganic constituents composing DARCO® FGD is presented in Table 6. The inorganic fraction of DARCO® FGD is primarily an Fe_2O_3-, CaO-, and SO_3-rich aluminosilicate material. It lacks alkali metals, Na_2O and K_2O, but contains relatively high alkaline-earth metal, CaO and MgO, contents.

Amended Silicate. ADA Technologies, Inc., through funding from EPA and DOE, has developed Amended Silicate™ sorbents using a commodity substrate material impregnated with a chemical amendment that binds Hg to the particle surface. Butz and others (22) claim that

Table 5. Physical and Chemical Characteristics of DARCO® FGD

Property or Characteristic, unit	Value
Moisture, wt% as received	8
Particle Size <325 mesh (45 µm), wt%	95
Iodine Number, mg/g	600
Bulk Density, tamped, g/mL	0.53
Surface Area, m^2/g	600
Total Sulfur, wt%	1.8
Ignition Temperature, °C (°F)	450 (842)

Table 6. Elemental Oxide Composition of DARCO® FGD

Elemental Oxide	Concentration, ash wt%
SiO_2	38.5
Al_2O_3	15.6
Fe_2O_3	10.6
TiO_2	1.3
P_2O_5	<0.1
CaO	18.1
MgO	4.7
Na_2O	0.7
K_2O	0.6
SO_3	10.0
Total	100.1

the Amended Silicate™ is cost-competitive with activated carbon and, unlike activated carbon, it does not hinder the salability of fly ash as a concrete additive. Testing on a flue gas slipstream at a power plant burning PRB subbituminous coal indicated that Amended Silicate™ sorbents provided 70%–96% Hg removal at injection rates of 1.6–9 lb/Macf (22).

EERC-Treated FGD. The EERC has developed a more effective activated carbon for capturing Hg using a proprietary chemical pretreatment process. Previous testing of the EERC-treated FGD on North Dakota lignite combustion flue gases has demonstrated that it is a much more effective Hg sorbent than DARCO® FGD (23).

Hg^0 Oxidation and Sorbent Enhancement Additives

Inorganic Chloride Compounds. Two commercially available inorganic chloride compounds, sodium chloride (NaCl) and calcium chloride ($CaCl_2$), were evaluated as Hg^0 oxidation and sorbent enhancement additives. The chemical compositions of these compounds are presented in Table 7. During combustion, these compounds will thermally decompose, and most of the Cl released will react with water vapor to produce HCl. It is also anticipated that some of the volatilized Cl will recombine with Na and Ca to form NaCl and $CaCl_2$. A very small proportion of the Cl is anticipated to remain in its atomic form, react to form HOCl or, through catalysis reactions with metals, form Cl_2. Theoretically, Cl, HOCl, and Cl_2 are chemically reactive with Hg^0 (24–26). In addition, Cl attached to a catalytic site on fly ash or carbon (unburned carbon or injected activated carbon) surfaces can oxidize Hg^0 and enhance Hg capture (27). $CaCl_2$ may be more effective in converting Hg^0 to Hg^{2+} and/or Hg(p) on an equal-addition-rate basis, because it contains more Cl relative to NaCl (Table 7).

SEA2. The EERC has identified an inorganic halide compound that effectively promotes the formation of Hg^{2+} and Hg(p) as well as enhances sorbent mercury capture performance. The chemical composition of this compound is currently not being reported because of proprietary concerns. This additive has been termed SEA2.

Table 7. Chemical Compositions of Chloride Compounds, wt%

Component	NaCl	CaCl$_2$
Na	39.34	NA
Ca	NA	36.11
Cl	60.66	63.89

Pilot-Scale Combustion System

Pilot-scale Hg control testing was conducted December 8–11, 2003, using a 580-MJ/hr (550,000-Btu/hr) pc-fired unit equipped with a Niro Inc. Production Minor Spray Dryer Model I and baghouse. This unit, shown schematically in Figure 20, is designed to generate fly ash and flue gas representative of that produced in a full-scale utility boiler. The combustor is oriented vertically to minimize wall deposits. A refractory lining helps to ensure adequate flame temperature for complete combustion and prevents rapid quenching of the coalescing or condensing fly ash. Based on the superficial gas velocity, the mean residence time of a particle in the combustor is approximately 3 seconds. The coal nozzle fires axially upward from the bottom of the combustor, and secondary air is introduced concentrically to the primary air with turbulent mixing. Coal is introduced to the primary air stream via a screw feeder and eductor. An electric
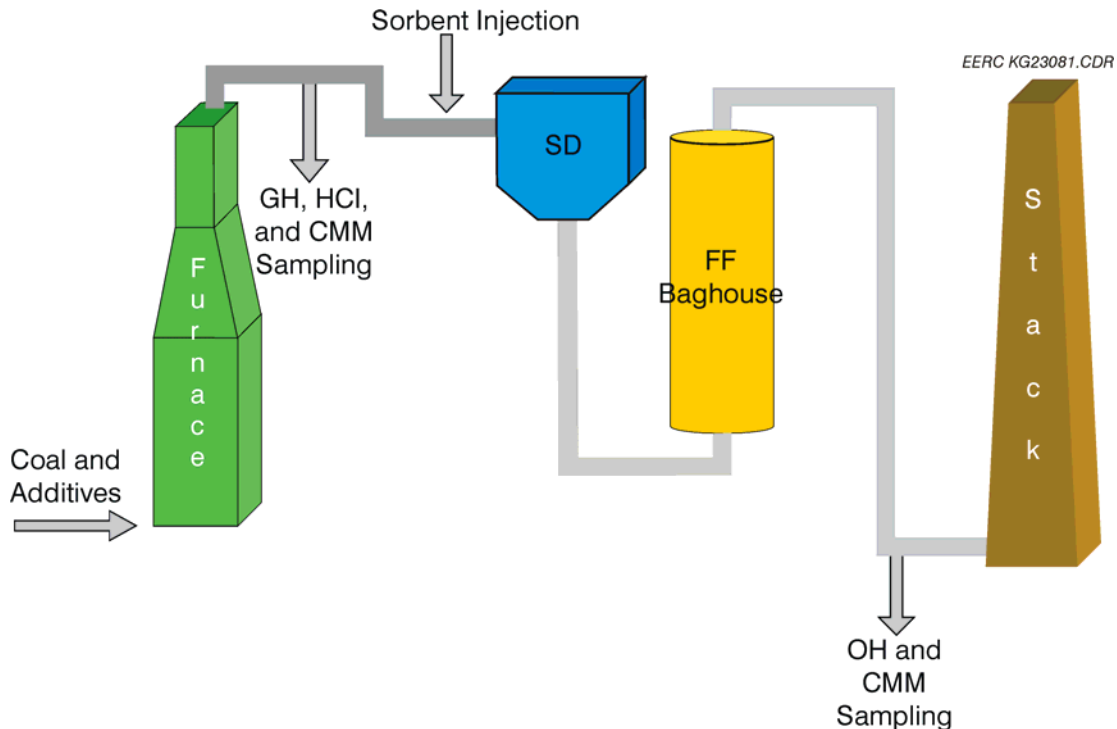
Figure 20. Schematic of the 580-MJ/hr (550,000-Btu/hr) combustion unit equipped with a FF and Niro Inc. Production Minor Spray Dryer, Model I.

air preheater is used for precise control of the combustion air temperature. Instrumentation enables system temperatures, pressures, flow rates, flue gas constituent concentrations, and PCD operating data to be monitored continuously and recorded on a data logger.

Niro Inc. Production Minor Spray Dryer, Model I

The SDA is shown schematically in Figure 21. The drying chamber is 1.2 m (3.9 ft) in diameter, with a 0.75-m (2.5-ft) cylindrical height and a 60° conical bottom. The inner shell is constructed of 2-mm stainless steel, Type AISI 316, with a 220-grit finish. A Niro Inc. Type FS-1 rotary atomizer, capable of speeds ranging from 10,500 to 30,000 rpm, was used for atomizing lime slurry. An air disperser, supplied with the rotary atomizer, was used to introduce the proper heated (149°C, 300°F) airflow pattern throughout the chamber.

The lime slurry for the SDA was prepared by adding deionized distilled water to slaked lime and fly ash obtained from the Antelope Valley Station in North Dakota. High-purity water was used to avoid the unintended introduction of chlorine into the system via a chlorinated water supply. Lime slurry compositions are presented in Table 8. The solid contents of the prepared slurries averaged 38 wt% on December 8 and 9 and 33 wt% on December 10 and 11.

Pilot-Scale Fabric Filter

The FF vessel (baghouse) is a heat-traced and insulated 20-in.-i.d. chamber. Flue gas enters the bottom of this chamber. The pilot-scale combustor produced about 200 acfm of flue gas at
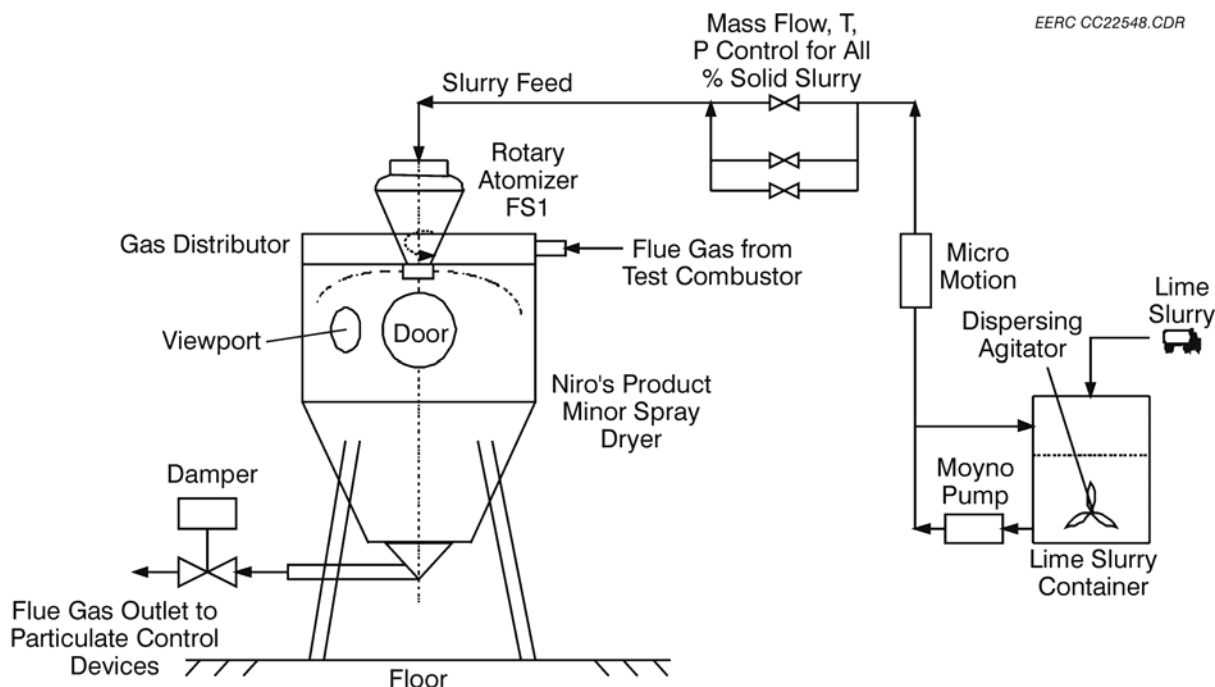
Figure 21. Schematic (not drawn to scale) of the Niro Inc. Production Minor Spray Dryer, Model I.

Table 8. Lime Slurry Compositions, wt%

Component	December 8 and 9, 2003	December 10 and 11, 2003
Ca(OH)$_2$	4	4
Fly Ash	34	29
Distilled Water	62	67

149°C (300°F), thus three 4-m by 2-cm (13-ft by 5-in.) polytetrafluoroethylene (PTFE) bags provided an air-to-cloth ratio of 1 m/min (4 ft/min). Each bag was cleaned separately with its own diaphragm pulse valve. Once bag cleaning was initiated, all three bags were pulsed in rapid succession online.

Mercury Control Test Conditions

A North Dakota lignite from the Center Mine, described in Table 9, was burned in the pilot-scale combustion system to test various Hg control strategies. The Center Mine is located in an extensive Tertiary basin Great Plains coal area which is centered in North Dakota and Montana and extends northward into Saskatchewan and southward into Wyoming and South Dakota. The coal combustion flue gas was cooled to approximately 149°C (300°F) before entering the SDA and FF. Nine tests were completed to evaluate the effectiveness of potential Hg sorbents (DARCO® FGD, EERC-treated FGD, and Amended Silicate™) and Hg^0 oxidation and sorbent enhancement additives (NaCl, SEA2, and CaCl$_2$) to remove Hg using a SDA and FF. The test matrix is presented in Table 10. As indicated in Figure 21, potential Hg^0 oxidation and sorbent enhancement additives were metered into the coal using a screw feeder prior to combustion, whereas the Hg sorbents were metered with a K-Tron dual-screw feeder upstream of the SDA.

Coal Analyses

A representative sample of lignite coal from the Center Mine was pulverized to a standard combustion grind (i.e., 70%–80% of the coal particles <75 μm) for analysis and combustion testing purposes. Daily samples of coal were collected during the 4 days of testing, and these were eventually combined to provide a composite sample for analysis. Proximate and ultimate analyses were conducted on the composite coal sample using ASTM Methods D3172, D5142, and D3176. A Mitsubishi Model TOX-100 Total Chlorine Analyzer was used to perform the recently validated ASTM Method D6721-01"Standard Test Method for Determination of Chlorine in Coal by Oxidative Hydrolysis Microcoulometry." Coal Hg content was determined

Table 9. Lignite Coal Information

Organization	Mine	Coal	Location	Mine Production[1], tons
BNI Coal Ltd.	Center	Hagel and Kinneman Creek	Western, Northern Lignite Basin, North Dakota, United States	4,415,033

[1] 2000 mine production statistic from *Keystone Coal Industry Manual*, Coal Age, PRIMEDIA Business Magazines & Media: Chicago, Illinois, 2002, 736 pp.

Table 10. Mercury Control Test Matrix

Coal Additive	Feed Rate, lb/Macf	Sorbent	Injection Rate, lb/Macf
None	NA	None	NA
None	NA	DARCO$^®$ FGD	1.84, 3.67, 7.35, and 11.0
None	NA	EERC-treated FGD	1.84, 3.67, and 7.35
None	NA	Amended Silicate™	7.35
NaCl	3.67, 7.35, and 11.0	None	NA
NaCl	3.67, 7.35, and 11.0	DARCO$^®$ FGD	3.67
SEA2	1.84 and 3.67	None	NA
SEA2	1.84 and 3.67	DARCO$^®$ FGD	1.84
CaCl$_2$	3.67, 7.35, and 11.0	None	NA
CaCl$_2$	3.67, 7.35, and 11.0	DARCO$^®$ FGD	3.67

in triplicate using cold-vapor atomic absorption spectroscopy according to EPA Method 245.1 and EPA SW-846 Method 7470.

Flue Gas Analyses

Continuous emission monitors (CEMs) were used to measure NO_x, NO, SO_2, O_2, CO, and CO_2 simultaneously at the SDA inlet and FF outlet. NO_x was determined using two Thermoelectron chemiluminescent NO_x analyzers. The O_2 and CO_2 analyzers were made by Beckman, and the SO_2 analyzers were manufactured by DuPont. Each of these analyzers was regularly calibrated and maintained to provide accurate flue gas concentration measurements.

Two Tekran CMMs were used to measure Hg^0 and Hg(g) concentrations simultaneously at the SDA inlet and FF outlet locations to determine the Hg(g) removal efficiency of various control strategies designed to improve the mercury capture of the SDA–FF pollutant control system. Tekran's sampling system is constructed of Teflon$^®$ and quartz glass. The analyzer employs a system of parallel gold amalgamation cartridges that automatically alternate between adsorb and desorb cycles. Cold-vapor atomic fluorescence spectroscopy is used for detecting and quantifying Hg^0. An internal permeation source provided automatic recalibration. The fly ash-sampling components of an EPA Method 29 sampling train, a glass nozzle and probe and quartz-fiber filter maintained at the flue gas temperature, were used to obtain particle-free gas samples for CMM analysis. Although CMMs can only directly measure Hg^0 concentrations, the EERC has developed a proprietary flue gas-conditioning and conversion system that removes acid gases and transforms Hg^{2+} into Hg^0 so that Hg(g) can be quantified and gaseous Hg^{2+} concentrations can be estimated by difference (i.e., $Hg^{2+} = Hg[g] – Hg^0$). Summarized in Table 11 are the various species of Hg that were measured directly or estimated and their corresponding abbreviations used throughout this report. The validity of CMM measurements was evaluated using ASTM Method D6784-02 (Ontario Hydro method).

Table 11. Mercury Speciation Terminology and Abbreviations

Mercury Species	Abbreviation
Gaseous Elemental Mercury	Hg^0
Gaseous Inorganic Mercuric Compounds	Hg^{2+}
Particle-Associated Mercury	Hg(p)
Total Gaseous Mercury, includes Hg^0 and Hg^{2+}	Hg(g)
Total Mercury, includes Hg^0, Hg^{2+}, and Hg(p)	Hg(total)

During tests involving the addition of Cl-containing compounds, infrared spectroscopy (Model 15C HCl analyzer) combined with a Perma Pure GASS™ drying system was used to measure HCl concentrations at the SDA inlet. It is believed that this is the first time that such an instrument has been used to measure HCl on a nearly continuous basis in a coal combustion flue gas.

Results and Discussion

Coal and Combustion Flue Gas Compositions

Proximate and ultimate analysis results for the North Dakota Center Mine lignite are presented in Tables 12 and 13, respectively. The Hg and Cl contents of the Center lignite are presented in Table 14. Based on the proximate and ultimate analysis data, it was calculated that a pound of Center lignite coal would produce 125 scf of dry flue gas normalized to a 3.0% O_2 concentration. Theoretically, the Hg(total) and HCl concentrations of the Center lignite combustion flue gas should be 13.8 $\mu g/Nm^3$ and 1.59 ppmv, respectively (on a dry flue gas at 3.0% O_2 basis).

Presented in Figures 22 and 23 are hourly average O_2, CO_2, CO, NO_x, and SO_2 concentrations measured at the SDA inlet and FF outlet, respectively, as a function of testing time. Analysis results for December 8, 2003, are not presented because of a CEM data-recording error that occurred during the first day of testing. CO concentrations ranged from <50 to 145 ppmv, which is indicative of efficient coal combustion and thus very low concentrations of unburned carbon in the fly ash. SDA inlet SO_2 concentrations ranged from 438 to 854 ppm,

Table 12. Center Lignite Coal Proximate Analysis Results

Analysis Parameters	Concentration, as-received, wt%
Moisture	30.5
Volatile Matter	33.4
Fixed Carbon	29
Ash	7.19
Heating Value, Btu/lb	7330

Table 13. Center Lignite Coal Ultimate Analysis Results

Analysis Parameters	Concentration, as-received, wt%
Carbon	43.8
Hydrogen[1]	2.82
Nitrogen	0.83
Sulfur	0.84
Ash	7.19
Oxygen (by difference)[1]	14
Total Moisture	30.5

[1] Hydrogen and oxygen do not include H and O in sample moisture.

Table 14. Center Lignite Coal Hg and Cl Concentrations, moisture-free, ppm

Analysis Replicate	Hg	Cl
1	0.0935	18
2	0.0999	19
3	0.0964	18
Average	0.0966	19
Standard Deviation	0.0032	<1
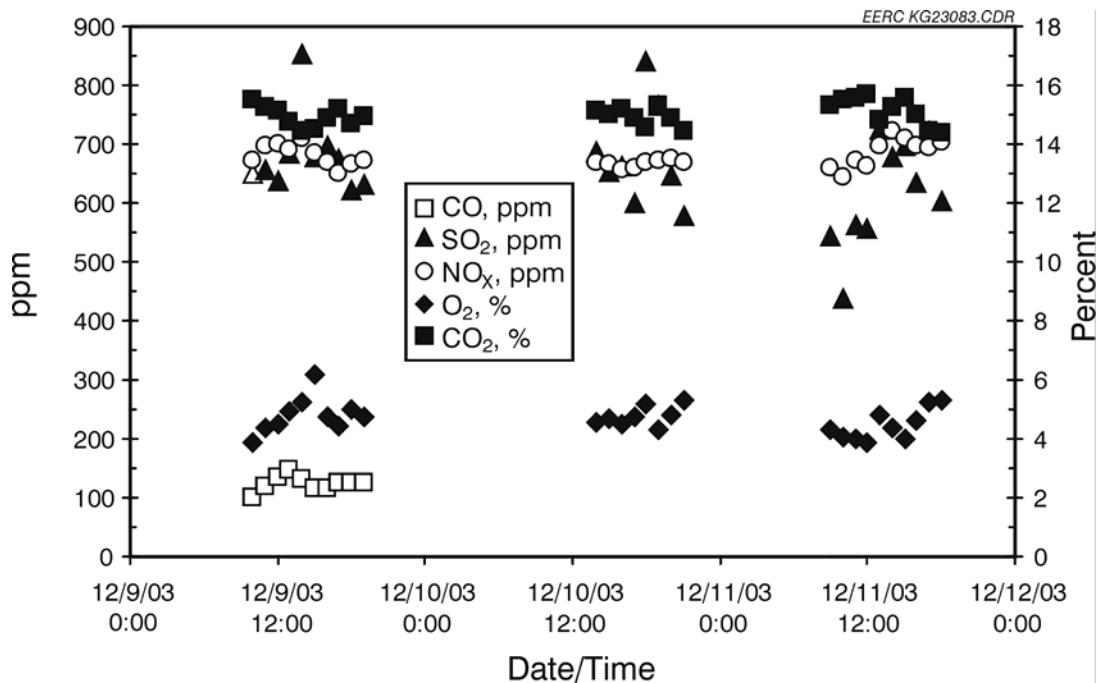
Figure 22. Hourly average Center lignite coal combustion O_2, CO_2, CO, NO_x, and SO_2 flue gas concentrations measured at the SDA inlet as a function of testing time.

Task 2
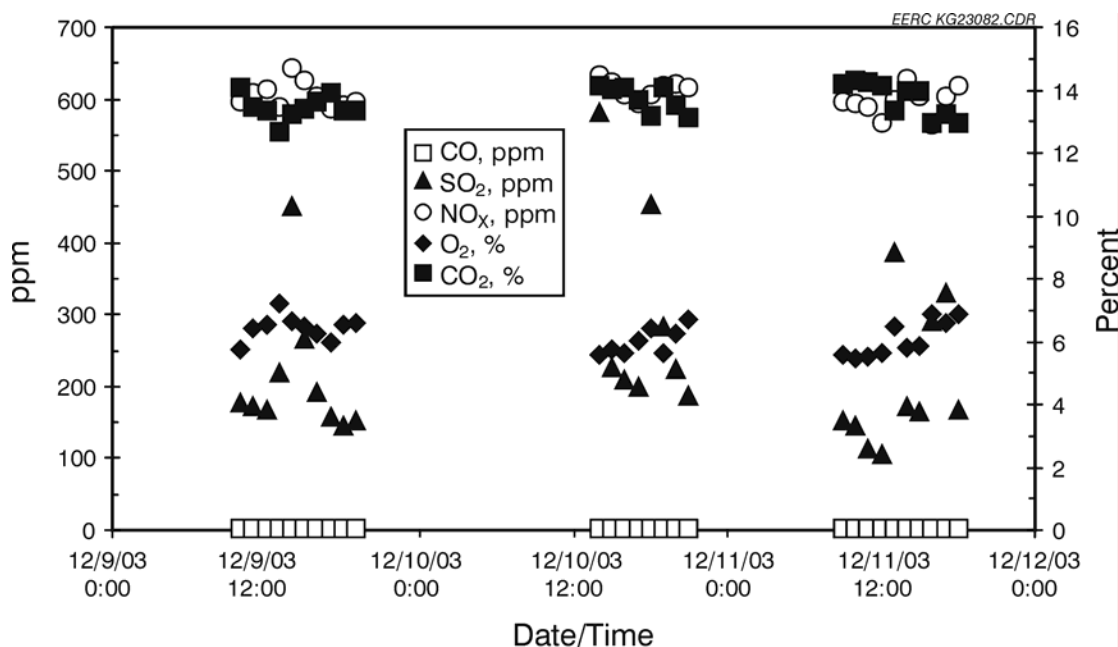
Figure 23. Hourly average Center lignite coal combustion O_2, CO_2, CO, NO_x, and SO_2 flue gas concentrations measured at the FF outlet as a function of testing time.

which is similar to the calculated SO_2 concentration, based on proximate and ultimate coal analysis (Tables 8 and 9), of 1010 ppmv (@ 6% O_2). The daily average SO_2 removal efficiencies of the SDA are reported in Table 15. Although the Center lignite combustion flue gas was anticipated to contain 1.59 ppmv HCl, it was not detected using infrared spectroscopy primarily because the Model 15C HCl analyzer was calibrated over a very wide range of HCl concentrations to accommodate the expected high HCl concentrations resulting from the addition of chloride compounds.

Evaluation of CMM Analysis Results

ASTM Method D6784-02 was performed three times at the SDA inlet and six times at the FF outlet during the mercury control testing to evaluate the validity of the CMM measurements. Compared in Figures 24, 25, and 26 are results that were obtained simultaneously using ASTM Method D6784-02 and a CMM. Figure 24 compares baseline CMM and ASTM Method D6784-02 analysis results that were obtained simultaneously during the combustion of Center coal at the SDA–FF inlet and outlet showing little mercury removal. A major limitation of the CMM measurements is that Hg(p) cannot be monitored. This limitation is most apparent in the

Table 15. Average Daily SO₂ Removal Efficiency of the SDA–FF

	December 9, 2003	December 10, 2003	December 11, 2003
Removal Efficiency, %	69.8	63.2	67.8
95% Confidence Limit, %	5.5	5.4	7.5

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results obtained at the SDA inlet (Figure 24), where there is more fly ash entrained in the flue gas. In addition, CMM measurement results for the SDA inlet were biased very low during tests involving NaCl and SEA2 additions because of the formation of Hg(p) upstream of the SDA inlet. Based on the comparisons in Figure 24, SDA inlet CMM results are generally not valid for calculating the Hg(g) removal efficiency of the SDA–FF, and this is more challenging when an effective Hg^0 oxidation and sorbent enhancement additive is used because much of the mercury is captured on the filter upstream of the analyzer. ASTM Method D6784-02 and CMM results show excellent agreement downstream from the FF, where Hg(g) concentration differences between the two methods were ≤6%(Figures 25 and 26).

Mercury Sorbent Performance

DARCO® FGD. Figure 27 illustrates the SDA inlet and FF outlet CMM results for Hg(g) and a calculated Hg(g) removal efficiency for each pair of CMM measurements that were conducted simultaneously or within a minute of each other. The results in Figure 27 are for the baseline Center lignite combustion flue gas and during the injection of DARCO® FGD at four different rates. The average Hg(g) removal efficiencies and corresponding 95% confidence limits were calculated from the results in Figure 27 and are presented in Table 16. Baseline results indicate that the SDA–FF was ineffective in removing Hg(g), with only 2.5% Hg removal. During DARCO® FGD injection, the Hg(g) removal efficiency of the SDA–FF improved immediately and continued to improve with increasing injection rates until it approached about 60% at an injection rate of 7.35 lb/Macf. The SDA–FF continued to remove Hg(g) after DARCO® FGD injection because of the presence of residual DARCO® FGD on the FF.
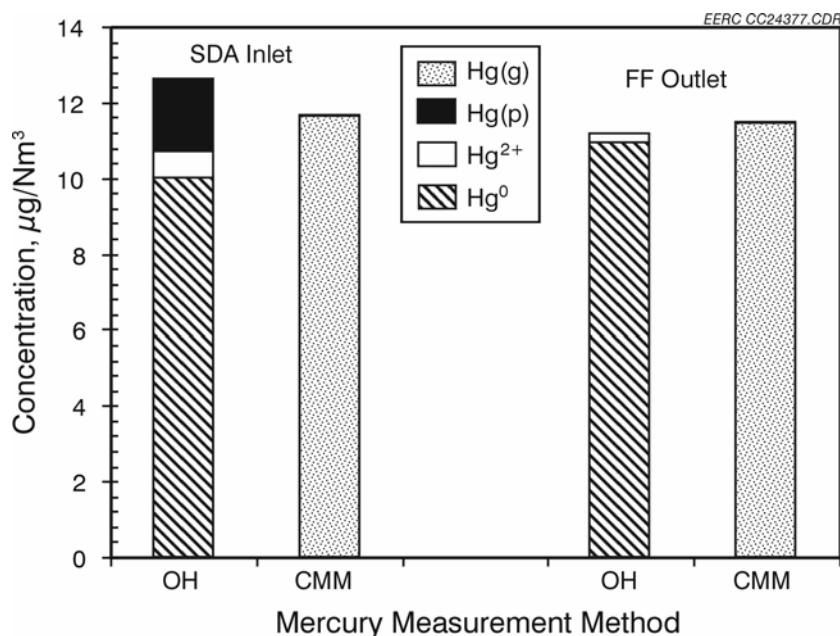
Figure 24. Comparison of average CMM and ASTM D6784-02 (OH method) Hg speciation results for baseline Center lignite combustion and SDA–FF tests.
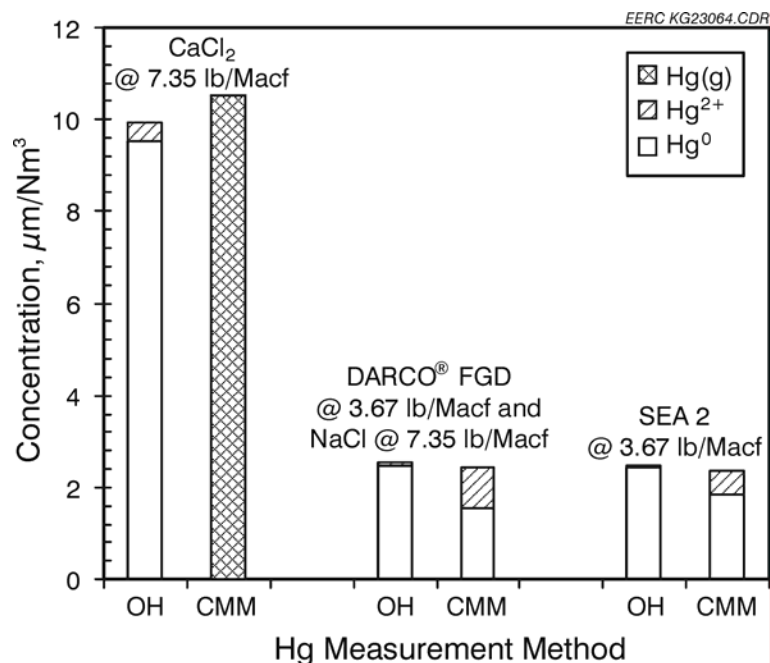
Figure 25. Comparison of ASTM Method D6784-02 (OH method) and CMM results obtained simultaneously at the FF outlet sampling location.
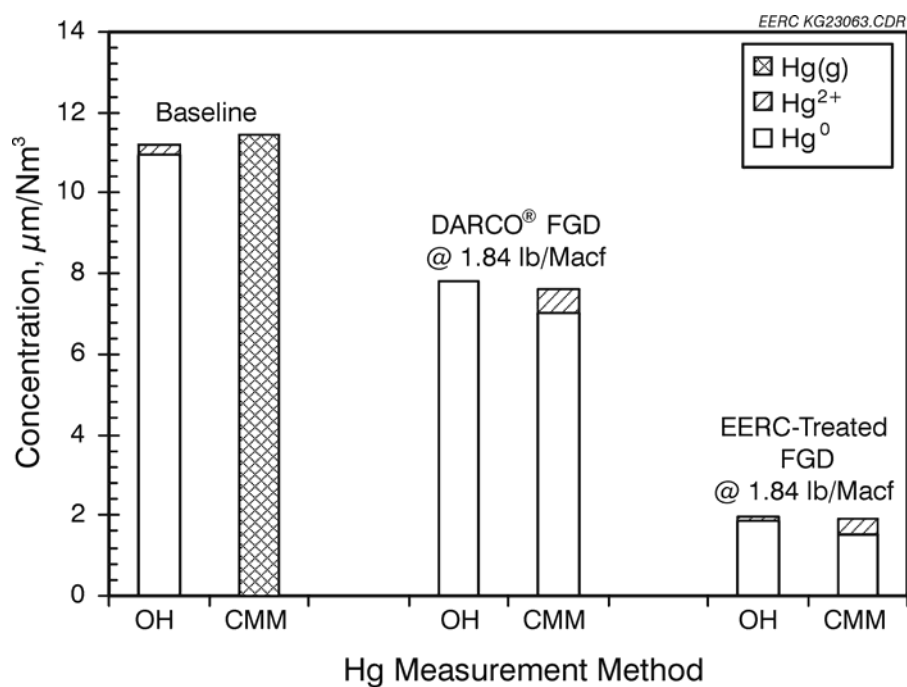
Figure 26. Comparison of ASTM Method D6784-02 (OH method) and CMM results obtained simultaneously at the FF outlet sampling location.
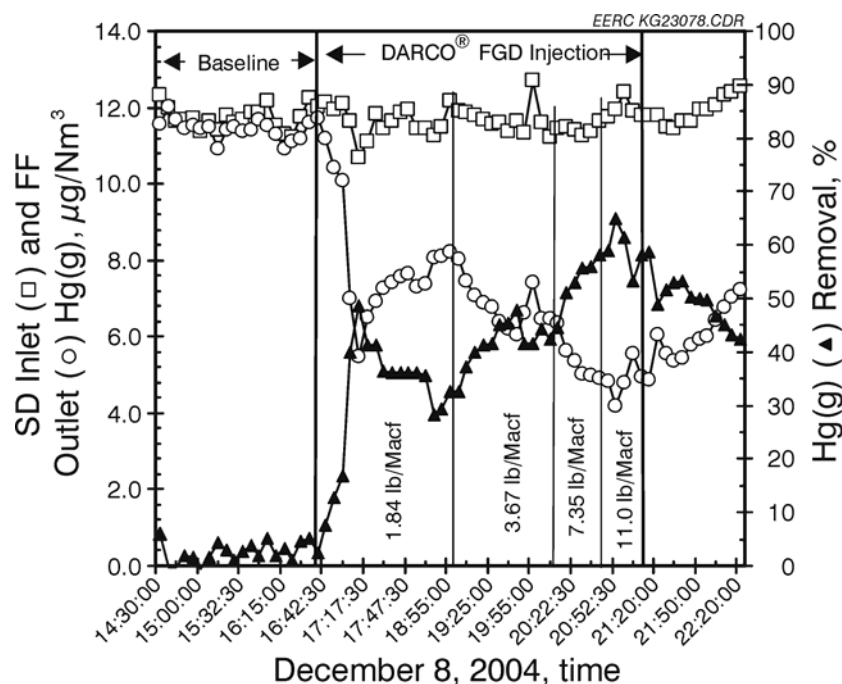
Figure 27. Paired SDA inlet and FF outlet CMM results and SDA–FF Hg(g) removal efficiencies for baseline and DARCO® FGD containing Center lignite coal combustion flue gas.

Table 16. SDA–FF Hg(g) Removal Efficiencies (%) Before and After DARCO® FGD Injection

Injection Rate, lb/Macf	0	1.84	3.67	7.35	11
Average	2.5	36.5	43.2	55.5	59.3
±95% Confidence Limit	±0.82	±2.5	±1.3	±2.2	±3.4

EERC-Treated FGD. Plotted in Figure 28 are paired CMM SDA inlet and FF outlet results and SDA–FF Hg(g) removal efficiencies before, during, and after injections of EERC-treated FGD. Average Hg(g) removal efficiencies as a function of EERC-treated FGD injection rate are presented in Table 17. The baseline SDA–FF Hg(g) removal efficiencies in Figure 28 are significantly higher relative to those from the previous day of testing (Figure 27, Table 12), perhaps because some residual DARCO® FGD remained on the FF. The EERC-treated FGD provided very good Hg(g) capture even at a low injection rate of 1.84 lb/Macf. Increasing the injection rate to ≥3.67 lb/Macf slightly improved SDA–FF Hg(g) capture to over 90% removal.

Amended Silicate™. Presented in Figure 29 are CMM results and SDA–FF Hg(g) removal efficiencies for a test involving Amended Silicate™ injection at 7.35 lb/Macf into the Center lignite coal combustion flue gas. The FF outlet Hg(g) concentrations prior to the Amended Silicate™ injection are biased low because of a previous test involving NaCl addition to the coal. Even though the pilot-scale combustion system was burning Center lignite in the absence of NaCl for 42 minutes prior to testing the Amended Silicate™, residual Cl apparently remained in
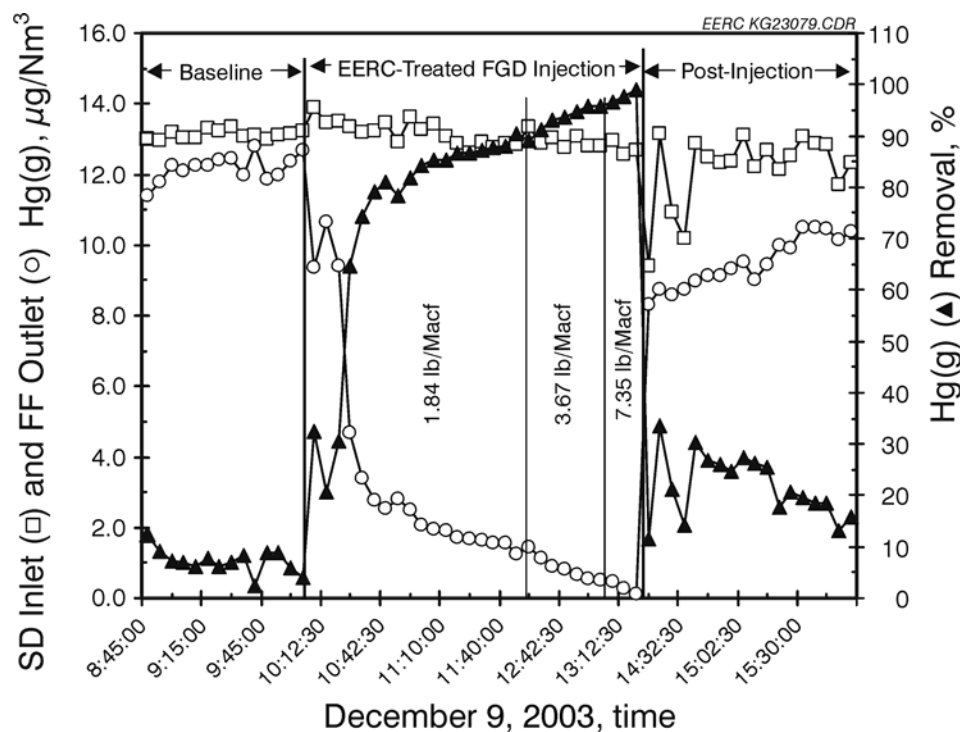
Figure 28. Paired SDA inlet and FF outlet CMM results and SDA–FF Hg(g) removal efficiencies for baseline and EERC-treated FGD containing Center lignite coal combustion flue gas.

Table 17. SDA–FF Hg(g) Removal Efficiencies (%) Before and After EERC-Treated FGD Injection

Injection Rate, lb/Macf	0	1.84	3.67	7.35
Average	7.2	85.1	94.4	98.3
±95% Confidence Limit	±1.22	±1.9	±1.3	NA[1]

[1] Not applicable because an insufficient number of analyses were made to calculate a value.

the system and enhanced SDA–FF Hg(g) removal. Hg(g) removal efficiencies during the Amended Silicate™ injection averaged 74.9% and were highly variable as evidenced by a 95% confidence limit of ±9.1%. The effectiveness of Amended Silicate™ to capture Hg(g) may have been enhanced by the presence of residual Cl in the system. After the injection of Amended Silicate™, the SDA–FF Hg(g) removal efficiency gradually returned to the level attained prior to testing the Amended Silicate™.
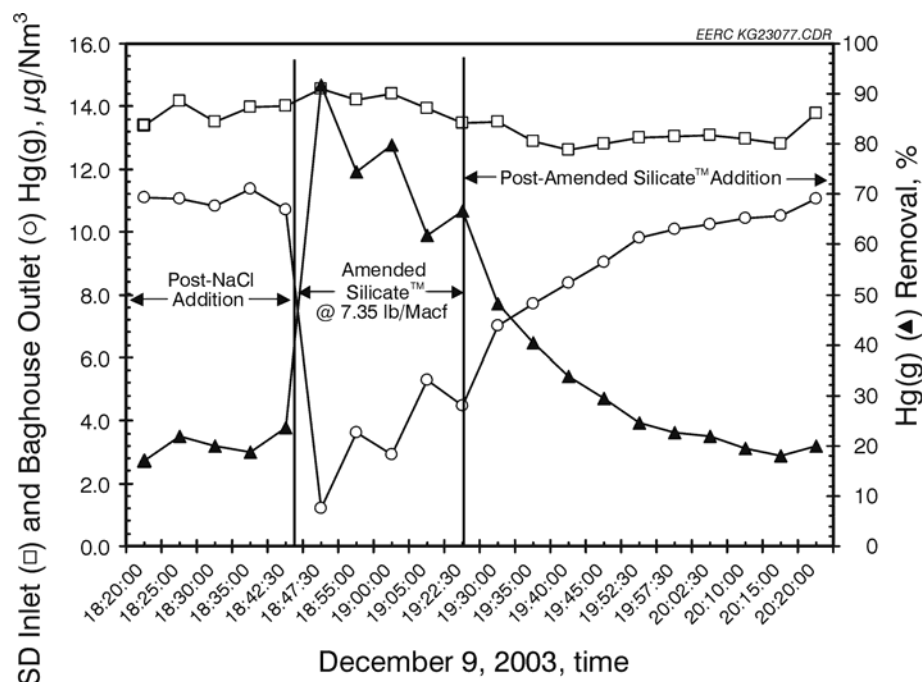
Figure 29. Paired SDA inlet and FF outlet CMM results and SDA–FF Hg(g) removal efficiencies before, during, and after the injection of Amended Silicate™ into the Center lignite coal combustion flue gas.

Mercury Sorbent Performance Comparison. Compared in Figure 30 are the average SDA–FF Hg(g) removal efficiencies for the three sorbents tested using Center lignite coal combustion flue gas. The size of the data points in Figure 30 is greater than the variability, at the 95% confidence level, of the Hg(g) removal efficiencies except in the case of Amended Silicate™ injection, where the variability was much greater as indicated by the error bar in Figure 30. Both the EERC-treated FGD and Amended Silicate™ sorbents outperformed DARCO® FGD, regardless of the injection rate.

Hg^0 Oxidation and Sorbent Enhancement Additive Performance

SEA1 (NaCl). The effects of adding NaCl to the Center lignite coal on flue gas Hg(g), Hg^0, and HCl concentrations are shown in Figure 31. The Model 15C HCl and CMM measurement results in Figure 31 were obtained from the SDA inlet and FF outlet locations, respectively. As expected, HCl concentrations increased significantly with the addition of NaCl to the Center lignite coal; however, Hg(g) concentrations only decreased slightly as the NaCl addition rate increased.

Presented in Figure 31 are the temporal variations in the FF outlet Hg(g) concentrations as NaCl was being added to the Center lignite coal. SDA inlet CMM results could not be used to calculate Hg(g) removal efficiencies because of a negative Hg(g) bias caused by NaCl–flue gas interactions that promoted Hg(p) formation. An average SDA inlet Hg(total) concentration determined from an ASTM Method D6784-02 measurement was used to calculate Hg(total)
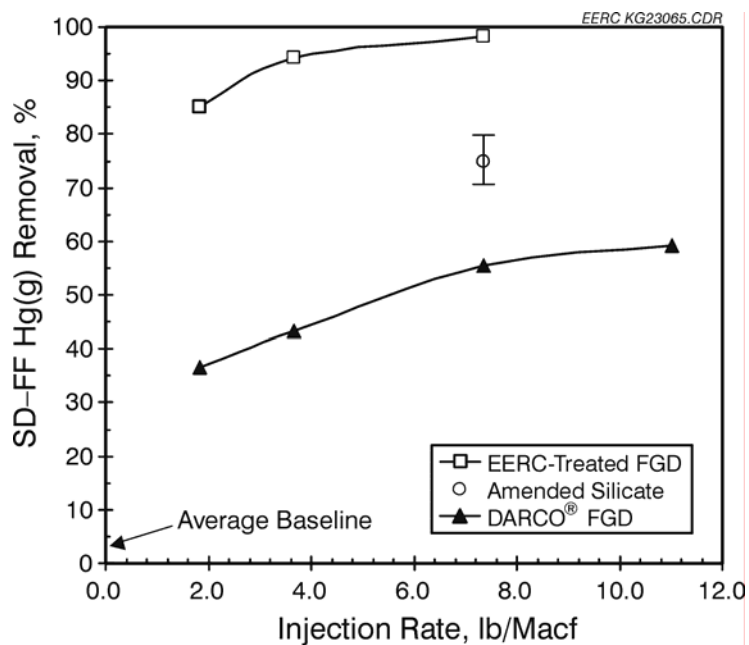
Figure 30. Comparison of SDA–FF Hg(g) removal efficiencies of mercury sorbents (DARCO®
FGD, EERC-treated FGD, and Amended Silicate™) as a function of injection rate. 95%
confidence limits are less than the size of a given data point unless denoted otherwise.

Figure 31. Temporal variations in SDA inlet HCl and FF outlet Hg(g) and Hg[0] concentrations as
NaCl was added to the Center lignite coal.

removal efficiencies shown in Figure 32. The ASTM Method D6784-02 SDA inlet Hg (total) results were very similar to the SDA inlet CMM Hg(g) measurement results obtained prior to the addition of NaCl; relative percent differences between the results were ≤3%. The average and variability of Hg(total) removal efficiencies presented in Table 16 are reported in Table 18. The FF outlet Hg(g) concentrations measured before the addition of NaCl are lower than typical baseline conditions, resulting in a Hg(total) removal of about 18%. Apparently, some residual EERC-treated FGD remained on the FF from the previous test. NaCl additions to the Center lignite coal improved SDA–FF Hg(total) capture. The total removal efficiency for NaCl addition only was 31.8% with 7.35lb/Macf NaCl added to the coal.
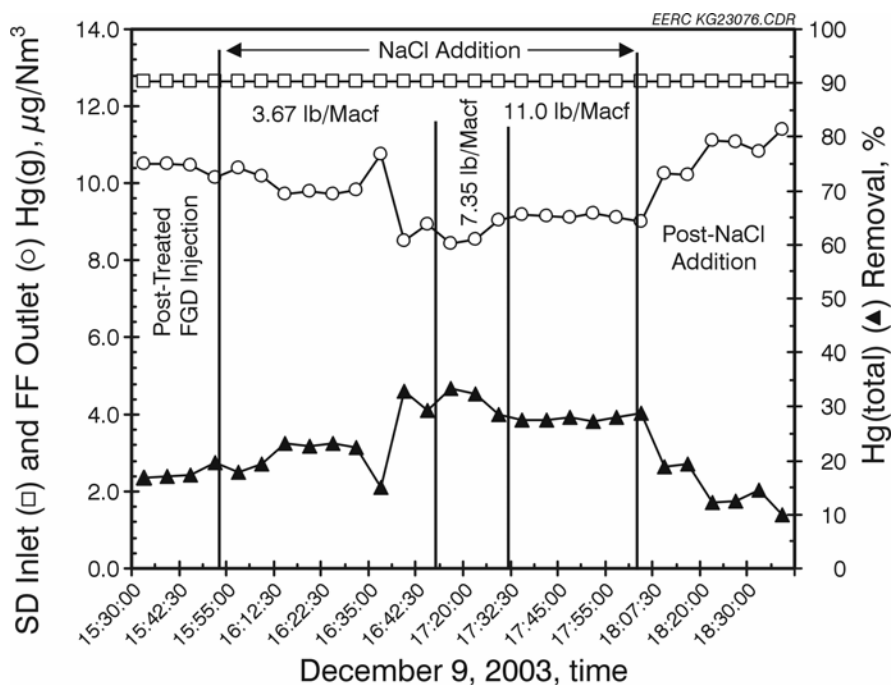
Figure 32. SDA inlet ASTM Method D6784-02 (OH method) and FF outlet CMM results and SDA–FF Hg(g) removal efficiencies before, during, and after the addition of NaCl into the Center lignite coal.

Table 18. SDA–FF Hg(total) Removal Efficiencies (%) Before and After NaCl Addition

Addition Rate, lb/Macf	0	3.67	7.35	11
Average	17.7	23.5	31.5	27.8
±95% confidence limit	±1.1	±3.6	±2.3	±0.4

Figure 33 illustrates the variations in SDA inlet HCl and FF outlet Hg(g) and Hg[0] concentrations during NaCl additions and DARCO® FGD injection at 3.67 lb/Macf into the Center lignite coal and combustion flue gas, respectively. The effect of NaCl additions on Hg(g) and Hg[0] concentrations are much more pronounced in the presence of DARCO® FGD as compared to the lone addition of NaCl (Figure 31). This indicates that the NaCl addition enhances the Hg(g) adsorption capacity of DARCO® FGD and, in the presence of carbon, may also increase the oxidation of Hg[0] more than the addition of NaCl alone. The oxidation of Hg[0] in the presence of carbon and small amounts of Cl has been reported in numerous laboratory studies (13–15). The synergistic effect of NaCl addition on DARCO® FGD Hg(g) capture and subsequent SDA–FF removal efficiency is shown in Figure 34. An average SDA inlet CMM Hg(g) value was used in Figure 34 when NaCl was being added because of the formation of Hg(p) upstream of the SDA inlet which negatively biased the CMM Hg(g) measurements. Figure 35 compares the average SDA–FF Hg(g) removal effectiveness of NaCl addition and DARCO® FGD injection alone and in combination. The combination of NaCl addition and DARCO® FGD injection is very effective in capturing Hg(g) in the SDA–FF PCDs.
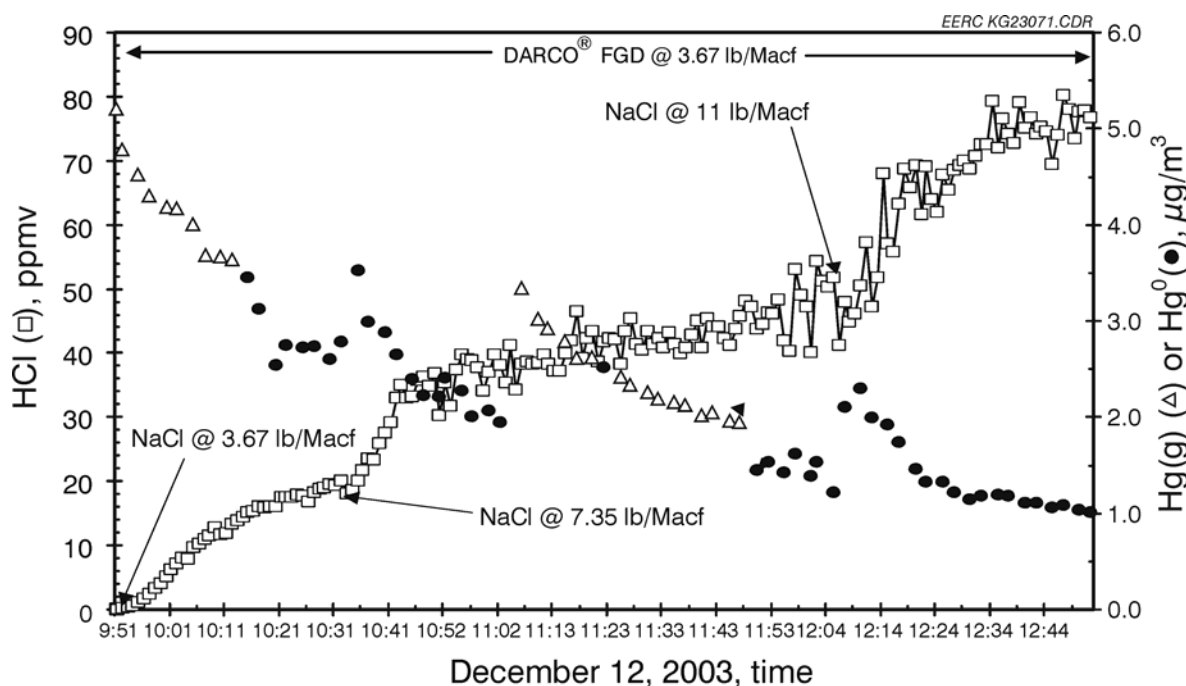
Figure 33. Temporal variations in SDA inlet HCl and FF outlet Hg(g) and Hg[0] concentrations during NaCl additions and DARCO® FGD injection at 3.67 lb/Macf.

Figure 34. SDA inlet and FF outlet CMM results and SDA–FF Hg(g) removal efficiencies before, during, and after NaCl additions and DARCO® FGD injection into the Center lignite coal and combustion flue gas, respectively.

Figure 35. Comparison of the average SDA–FF Hg(g) removal efficiencies of NaCl additions and DARCO® FGD injections alone and in combination. Variability at the 95% confidence level in the average values is approximately equivalent to the size of a given data point.

SEA1 (CaCl₂). Presented in Figures 36 and 37 are the temporal variations in SDA inlet HCl and FF outlet Hg(g) and Hg^0 concentrations associated with $CaCl_2$ additions and DARCO® FGD injection at 3.67 lb/Macf into the Center lignite coal and combustion flue gas, respectively. Similar to NaCl additions, $CaCl_2$ additions alone caused Hg(g) and Hg^0 concentrations to gradually decline with time and increasing $CaCl_2$ addition rates as shown in Figure 36. The combination of DARCO® FGD injection at 3.67 lb/Macf and $CaCl_2$ additions resulted in much greater reductions in FF outlet Hg(g) concentrations (Figure 37). Figure 38 shows the calculated SDA–FF Hg(g) removal efficiencies for pairs of SDA inlet and FF outlet CMM measurements made during $CaCl_2$ additions and DARCO® FGD injections. An average SDA inlet CMM Hg(g) value was used in Figure 38 when $CaCl_2$ was being added because of the formation of Hg(p) upstream of the SDA inlet, which negatively biased CMM Hg(g) measurements. The SDA–FF Hg(g) removal efficiencies in Figure 38 clearly demonstrate that the combination of $CaCl_2$ addition and DARCO® FGD injection provides much more effective Hg(g) emission control relative to $CaCl_2$ addition or DARCO® FGD injection alone. Figure 39 compares the average SDA–FF Hg(g) removal effectiveness of $CaCl_2$ addition and DARCO® FGD injection alone and in combination.
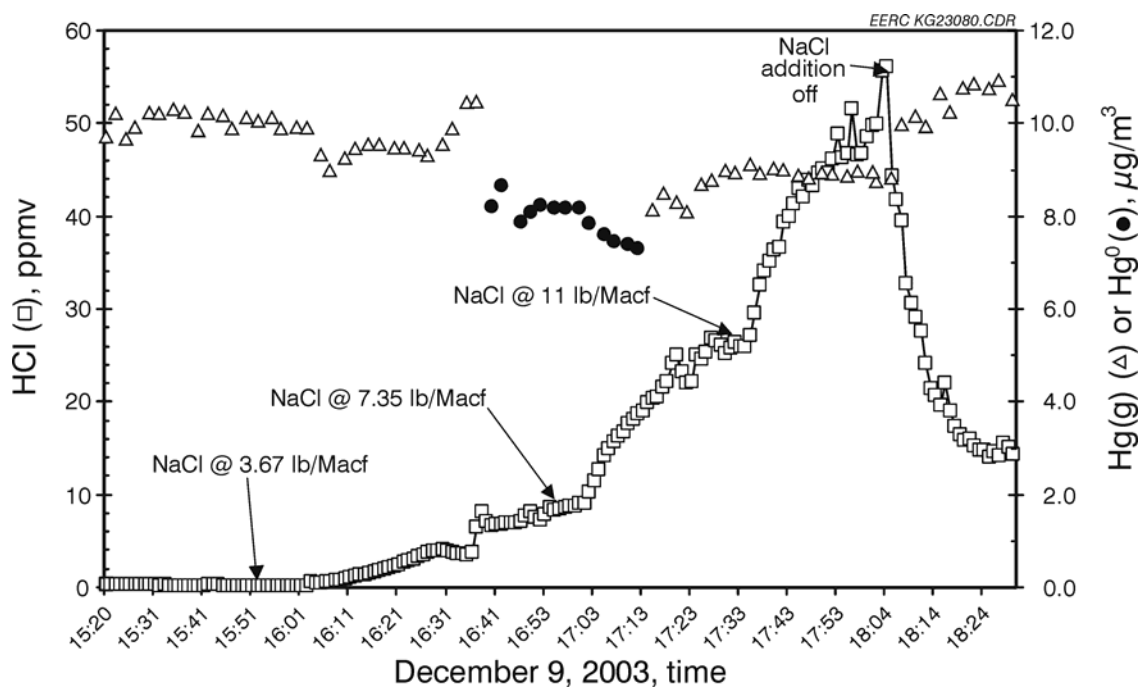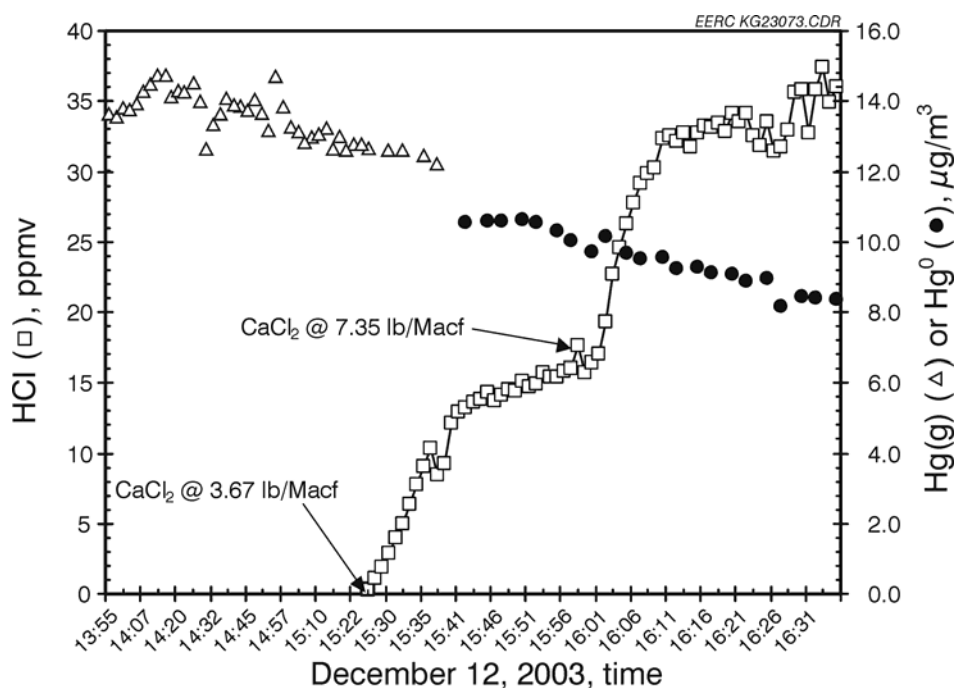

Figure 36. Temporal variations in SDA inlet HCl and FF outlet Hg(g) and Hg^0 concentrations during $CaCl_2$ additions to the Center lignite coal.
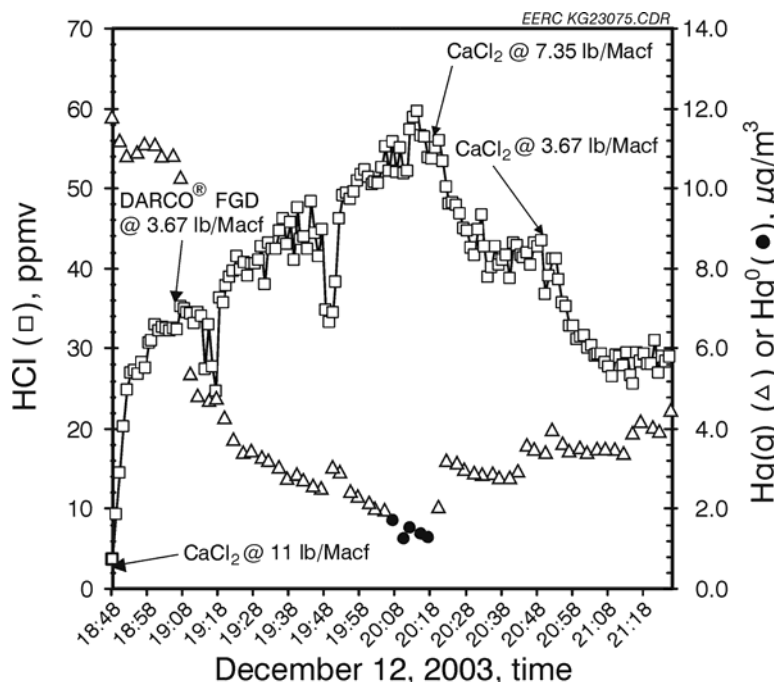
Figure 37. Temporal variations in SDA inlet HCl and FF outlet Hg(g) and Hg^0 concentrations during CaCl$_2$ additions and DARCO® FGD injection at 3.67 lb/Macf into the Center lignite coal and combustion flue gas, respectively.
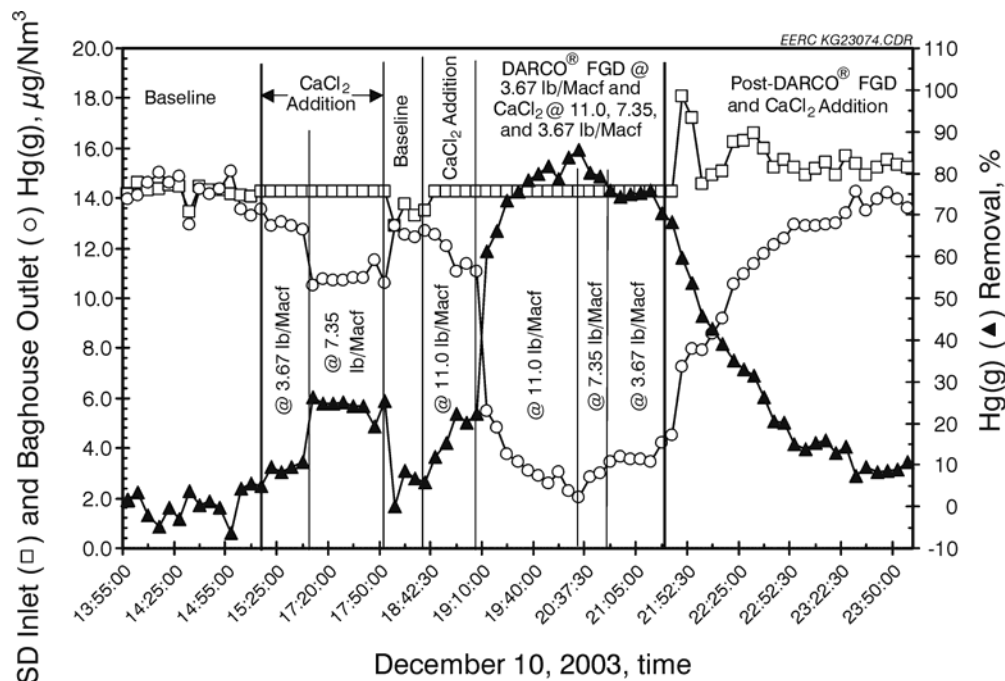
Figure 38. SDA inlet and FF outlet CMM results and SDA–FF Hg(g) removal efficiencies before, during, and after CaCl$_2$ additions and DARCO® FGD injection into the Center lignite coal and combustion flue gas, respectively.
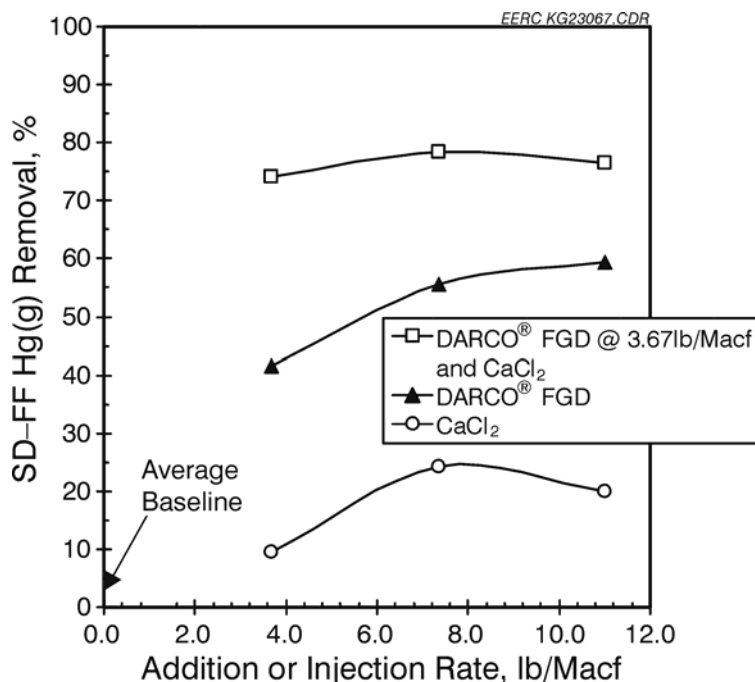
Figure 39. Comparison of the average SDA–FF Hg(g) removal efficiencies of CaCl₂ additions and DARCO® FGD injections alone and in combination. Variability at the 95% confidence level in the average values is approximately equivalent to the size of a given data point.

The results in Figure 39 are similar to those in Figure 35 for NaCl addition because the active component of both compounds that reacts with Hg^0 to produce Hg^{2+} and/or Hg(p) is the Cl anion.

SEA2. Figure 40 illustrates the calculated SDA–FF Hg(g) removal efficiencies for pairs of SDA inlet and FF outlet CMM measurements made during SEA2 additions and DARCO® FGD injection into the Center lignite coal and combustion flue gas, respectively. Similar to the NaCl and CaCl₂ addition tests, an average SDA inlet CMM Hg(g) value was used in Figure 40 when SEA2 was being added because of the formation of Hg(p) upstream of the SDA inlet, which negatively biased CMM Hg(g) measurements. The initial FF outlet Hg(g) concentrations measured before the addition of SEA2 are lower than typical baseline conditions, resulting in Hg(g) removal of about 17%. Apparently, some residual DARCO® FGD remained on the FF from the previous test (Figure 34). SEA2 greatly improved the Hg(g) removal effectiveness of the SDA–FF, especially at the greater addition rate of 3.67 lb/Macf. After SEA2 addition, the FF outlet Hg(g) concentration gradually increased over about a 30-min period to its pre-SEA2 addition concentration. The combination of DARCO® FGD injection at 1.84 lb/Macf and SEA2 addition provided exceptional SDA–FF Hg(g) capture, >90%, even at the lower addition rate of 1.84 lb/Macf. Compared in Figure 41 are the average SDA–FF Hg(g) removal efficiencies of SEA2 addition and DARCO® FGD injection alone and in combination. The size of the data points in Figure 41 are greater than the variability, at the 95% confidence level, of the SDA–FF Hg(g) removal efficiencies except in the case of SEA2 addition at 1.84 lb/Macf, where the variability was greater as indicated by the error bar in Figure 41.
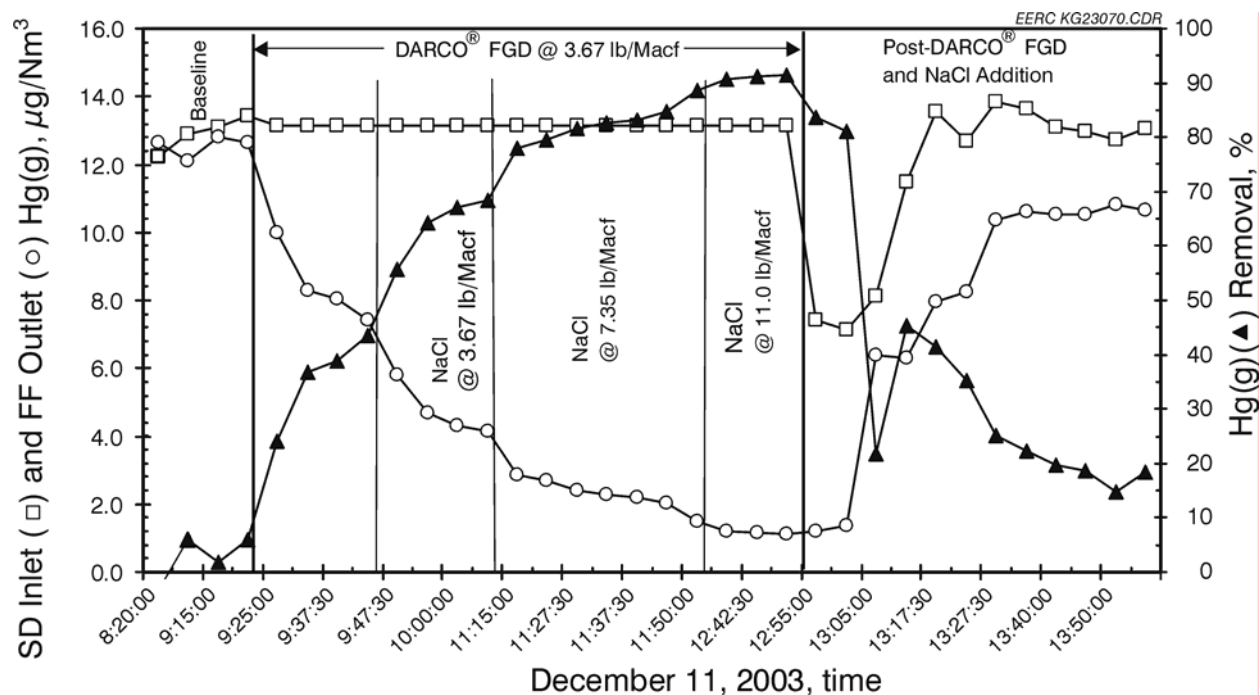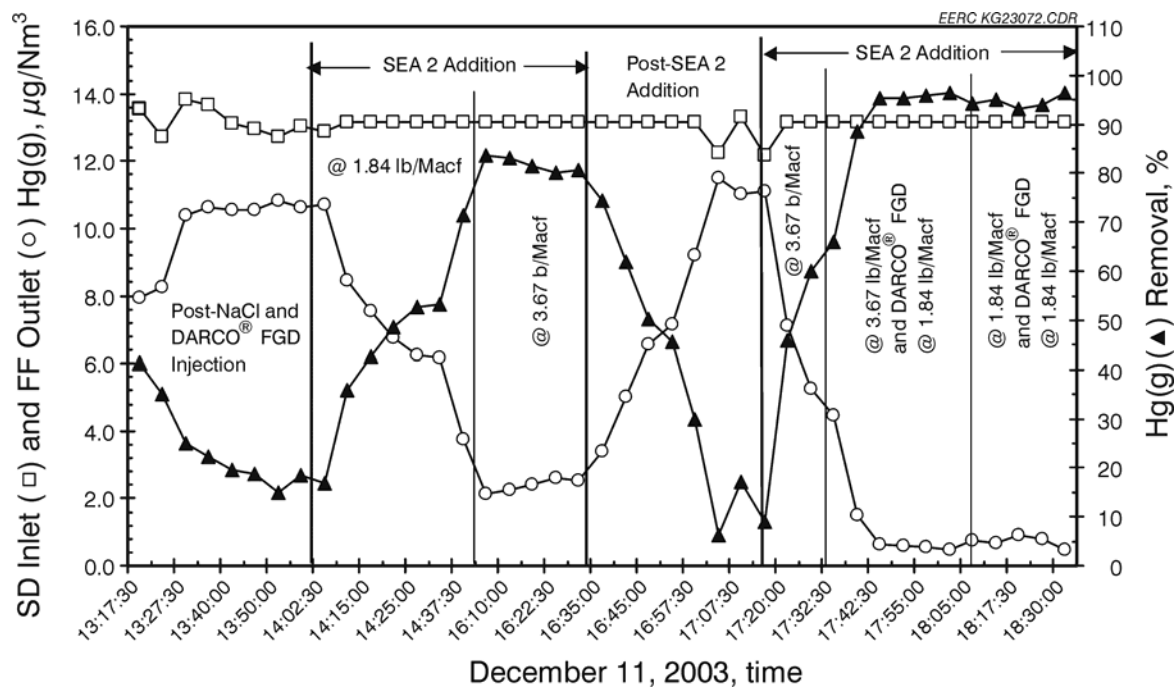
Figure 40. SDA inlet and FF outlet CMM results and SDA–FF Hg(g) removal efficiencies before, during, and after SEA2 additions and DARCO® FGD injection into the Center lignite coal and combustion flue gas, respectively.
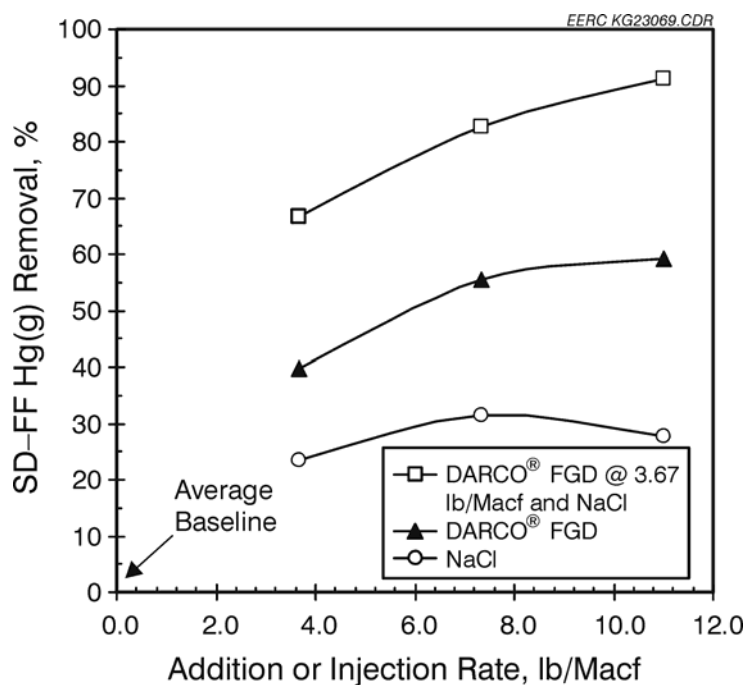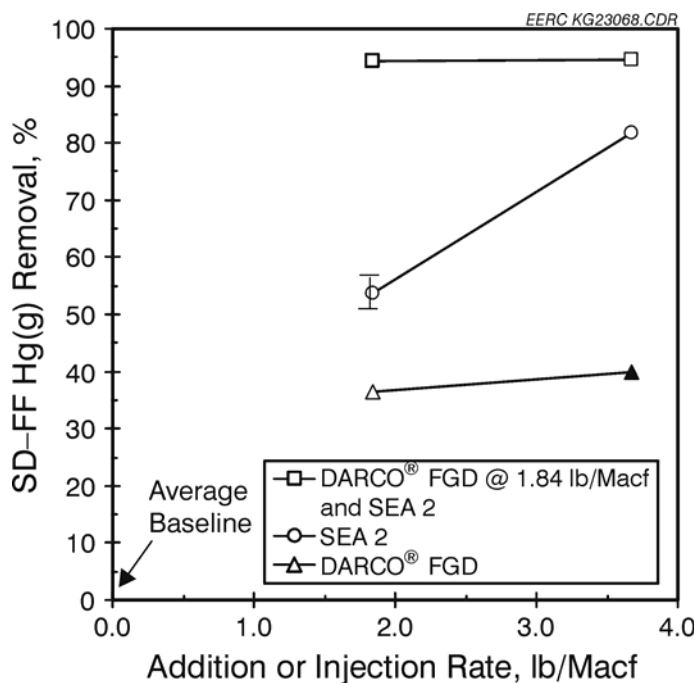

Figure 41. Comparison of the average SDA–FF Hg(g) removal efficiencies of SEA2 additions and DARCO® FGD injections alone and in combination.

Hg^0 Oxidation and Sorbent Enhancement Additive Performance Comparison. Figure 42 and Table 19 summarizes and compares the average SDA–FF Hg(g) removal efficiencies when NaCl, CaCl$_2$, and SEA2 additives were used with and without DARCO® FGD. The combination of SEA2 addition and DARCO® FGD injection provided the best SDA–FF Hg(g) removal efficiency, even at the lowest addition and injection rates of 1.84 lb/Macf. NaCl and CaCl$_2$ addition combined with DARCO® FGD injection provided similar high levels of SDA–FF Hg(g) removal, ≈70%–90%, although the lone addition of SEA2 at 3.67 lb/Macf also provided a similar level of efficient Hg(g) removal.
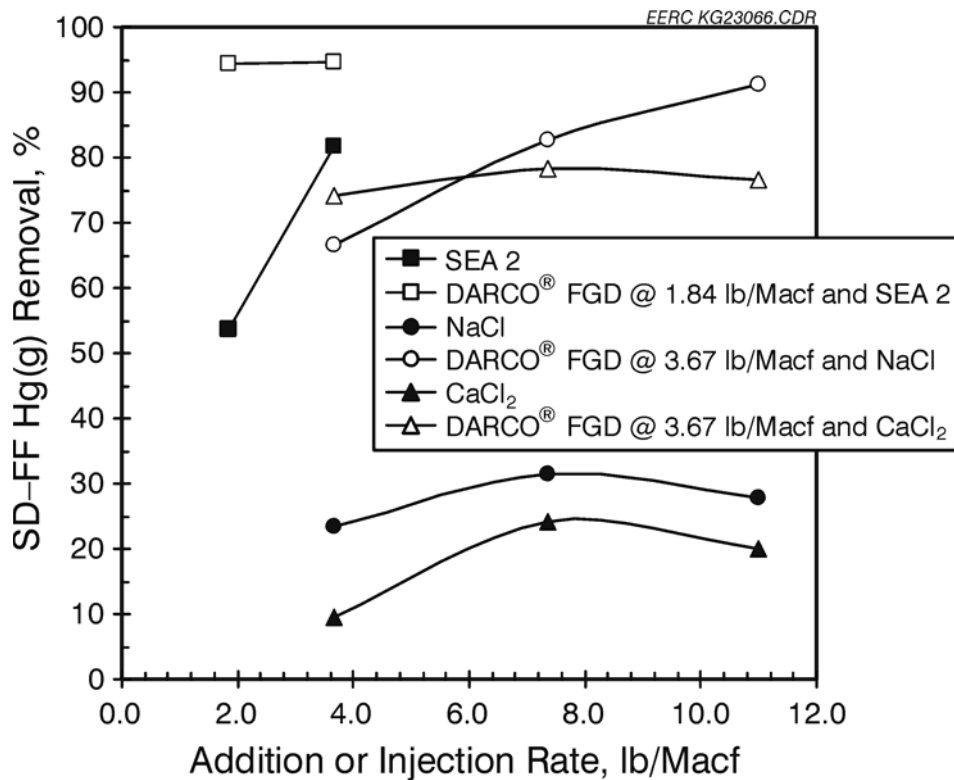
Figure 42. Comparison of the average SDA–FF Hg(g) removal efficiencies of NaCl, CaCl$_2$, and SEA2 additions alone and in combination with DARCO® FGD injection.

Table 19. Average ±95% confidence limit) SDA–FF Hg(g) Removal Efficiencies for Sorbents and Additives, %

Sorbent and/or Additive	Injection or Addition Rate, lb/Macf			
	1.84	3.67	7.35	11
DARCO® FGD	36.5 ±2.5	43.2 ±1.3	55.5 ±2.2	59.3 ±3.4
Amended Silicate™	NT[1]	NT	74.9 ±9.1	NT
EERC-treated FGD	85.1 ±1.9	94.4 ±1.3	98.3 ±NA[2]	NT
NaCl	NT	23.5 ±3.6	31.5 ±2.3	27.8 ±0.4
CaCl$_2$	NT	9.5 ±0.8	24.2 ±1.4	20.0 ±2.8
SEA2	53.7 ±5.3	81.8 ±1.2	NT	NT
DARCO® FGD @ 3.67 lb/Macf and NaCl	NT	66.6 ±2.4	82.6 ±2.4	91.2 ±0.5
DARCO® FGD @ 3.67 lb/Macf and CaCl$_2$	NT	74.2 ±1.7	78.4 ±2.1	76.5 ±4.5
DARCO® FGD @ 1.84 lb/Macf and SEA2	94.6 ±0.9	94.3 ±2 6	NT	NT

[1] Not tested.
[2] Not applicable because an insufficient number of analyses were made to calculate a value.

TASK 3 – FIELD TESTS TO DETERMINE IMPACTS OF OXIDIZING AGENTS ON MERCURY SPECIATION

The specific objective of this task is to enhanced oxidation at a full-scale power plant using tire-derived fuel (TDF) and oxidizing catalysts.

Experimental

Task 3.1 – Impacts of Cofiring on TDF

The efforts in this subtask were aimed at testing the ability of cofiring TDF with North Dakota lignite to increase the oxidized and particulate forms of Hg at a fluid bed-fired power plant (Montana–Dakota Utilities Heskett Station Unit 2, 85 MW, ESP). Testing included obtaining Hg speciation and removal information when firing 100% lignite at full load and up to 10% TDF (Btu basis). Mercury and Cl species levels in the flue gas phase were measured at the inlet and outlet of the ESP with and without cofiring the TDF. Coal and TDF were analyzed for basic proximate, ultimate, sulfur, and ash compositional analysis, Cl, Zn, and Hg. Total Hg collection efficiency of the ESP and the Hg speciation information were determined.

Task 3.2 – Impacts of Oxidation Catalysts – Coyote Station Slipstream Testing

The second subtask involved a literature review and summary of the state of mercury oxidation catalysts in place of the proposed testing of Hg oxidation agent in conjunction with a preexisting EERC project.

Results and Discussion

Task 3.1 – Impacts of Cofiring on TDF

Mercury sampling and measurements were performed at the inlet and outlet of the ESP at the Heskett Station with and without firing TDF. Auburndale Recycling provided approximately 100 tons of TDF to the Heskett Station. The TDF was fired at approximately 10% of the total heat input. Four OH samples were taken over a period of 2 days to determine the effect TDF has on Hg speciation/removal. Chlorine levels were also measured with EPA Method 26A with and without the TDF.

The proximate–ultimate, chlorine, and bulk chemistry analyses presented in Tables 20 and 21 were completed on both the TDF and the coal. The proximate–ultimate analyses indicated similar fixed carbon, hydrogen, nitrogen, sulfur, and ash content for both materials. The TDF had very little moisture (0.70%) and much higher volatile matter content (68.82%) as compared to the lignite coal. The chlorine content of the TDF was also much greater at 324 ppm than that of the coal at 7.4 ppm, which will impact the Hg speciation in the flue gas. The noteworthy differences in bulk chemistry were the high zinc and iron contents in the TDF versus the high calcium and silica contents of the coal. The TDF added little Hg to the system, as its Hg concentration was several orders of magnitude lower than the Hg in the coal.

Table 20. Properties of the Materials Cofired at Heskett Station, wt%[1]

	TDF, as-received	Beulah Lignite Coal, as-received
Moisture	0.70	35.70
Volatiles	68.82	29.41
Fixed Carbon	26.34	28.47
Ash	4.14	6.42
Hydrogen	7.68	6.77
Carbon	83.48	41.35
Nitrogen	0.78	0.77
Sulfur	1.55	0.58
Oxygen	2.37	44.11
Ash	4.14	6.42
Heating Value	15805 Btu/lb	6850 Btu/lb
Mercury	0.0094 ppm	0.04 ppm
Chlorine	324 ppm	7.4 ppm

[1] Unless otherwise noted.

Table 21. Bulk Chemistry Analysis of the Ashed Material Cofired at Heskett Station, wt%[1]

	TDF, as-received	Beulah Coal, as-received
Na_2O	9.97	10.55
MgO	1.33	6.75
Al_2O_3	9.4	13.9
SiO_2	16.3	25.4
P_2O_5	0.62	0.4
SO_3	9.7	15.09
K_2O	0.86	0.61
CaO	3.8	20.6
Fe_2O_3	14.66	6.24
TiO_2	4	0.42
ZnO	29.2	ND[2]

[1] Unless otherwise noted.
[2] Not determined (excellent closure for the elements detected indicates that very little if any zinc would be present).

The Hg partitioning in the flue gas is presented in Figure 43. Under baseline coal-fired conditions, approximately 15% of the Hg at the inlet of the ESP was in the elemental form. The ESP removed about 50% of the Hg in the system, leaving about 95% Hg^0 at the stack. With the addition of TDF to the fuel, the amount of Hg at the ESP inlet was about 6 μg/m^3, with about 5% in the elemental form. The ESP removed about 80% of the total Hg while firing TDF, with 90% of the remaining Hg in the elemental form. The high level of chlorine in the TDF is likely the reason for the increase in Hg removal across the ESP.
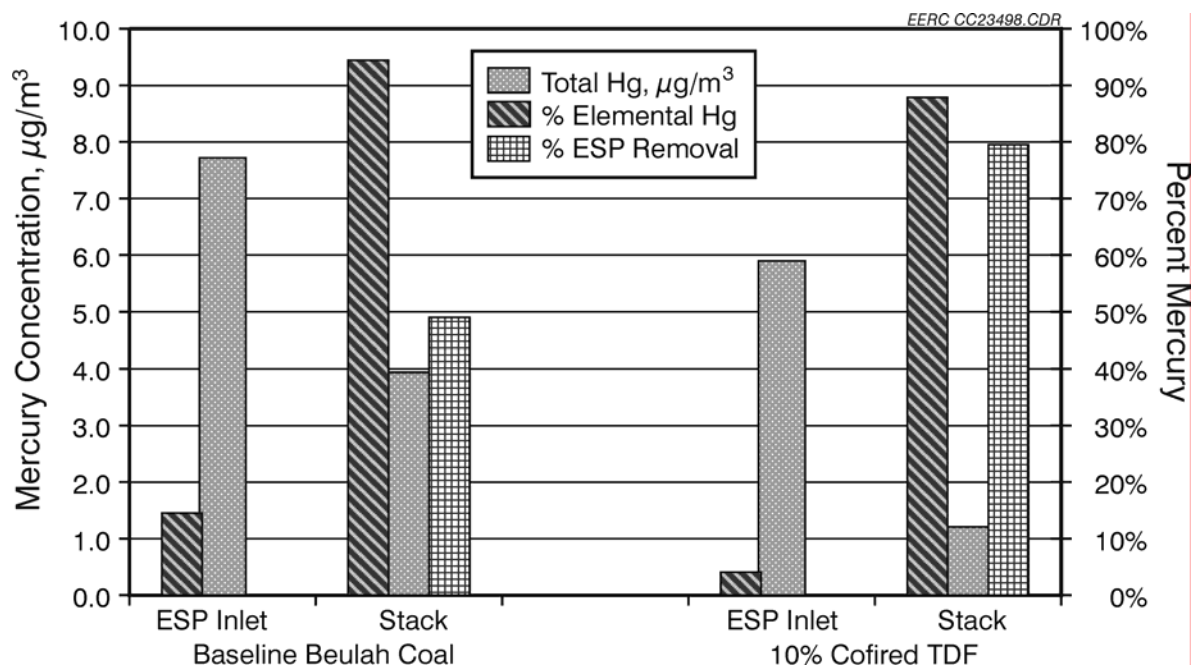
Figure 43. Mercury concentration and partitioning during OH method sampling at the ESP inlet and stack under baseline coal-fired and TDF cofired conditions at Heskett Station (April 2004).

Figure 44 contains the results of the chlorine measurements taken during the same sampling period as the OH Hg samples. It is interesting to note that the chlorine concentration at the stack and the inlet to the ESP were lower while firing TDF. A possible explanation is that the extra chlorine added to the system was taken up by the calcium-rich bed material. No ash samples were collected during the testing; therefore this hypothesis cannot be tested. Future studies using fluidized-bed combustion systems and TDF should include sufficient analysis of the bed and ash material.

Task 3.2 – Impacts of Oxidation Catalysts – Coyote Station Slipstream Testing

The oxidation catalyst testing was not conducted. We were not able to resolve intellectual property issues with the catalyst vendor before the SCR system had to be removed from the Coyote Station. In place of the oxidation catalyst work, a summary on the state of oxidation catalysts as well as EERC experience with lignite and SCR systems is included below.

Previous work conducted by the EERC at the Coyote Station has shown little to no Hg oxidation across SCR catalyst while firing lignite coal. The study was conducted over a period of 6 months, with OH measurements taken every 2 months at the inlet and outlet of an SCR slipstream system. Figure 45 is a graphical representation of the data collected from the SCR at the Coyote Station after 6 months of operation. These data are representative of all the sampling periods conducted during the project. It was also discovered during this project that ammonia present in the SCR system has an effect on Hg speciation. With ammonia on, the amount of oxidized Hg was lower than without the ammonia.
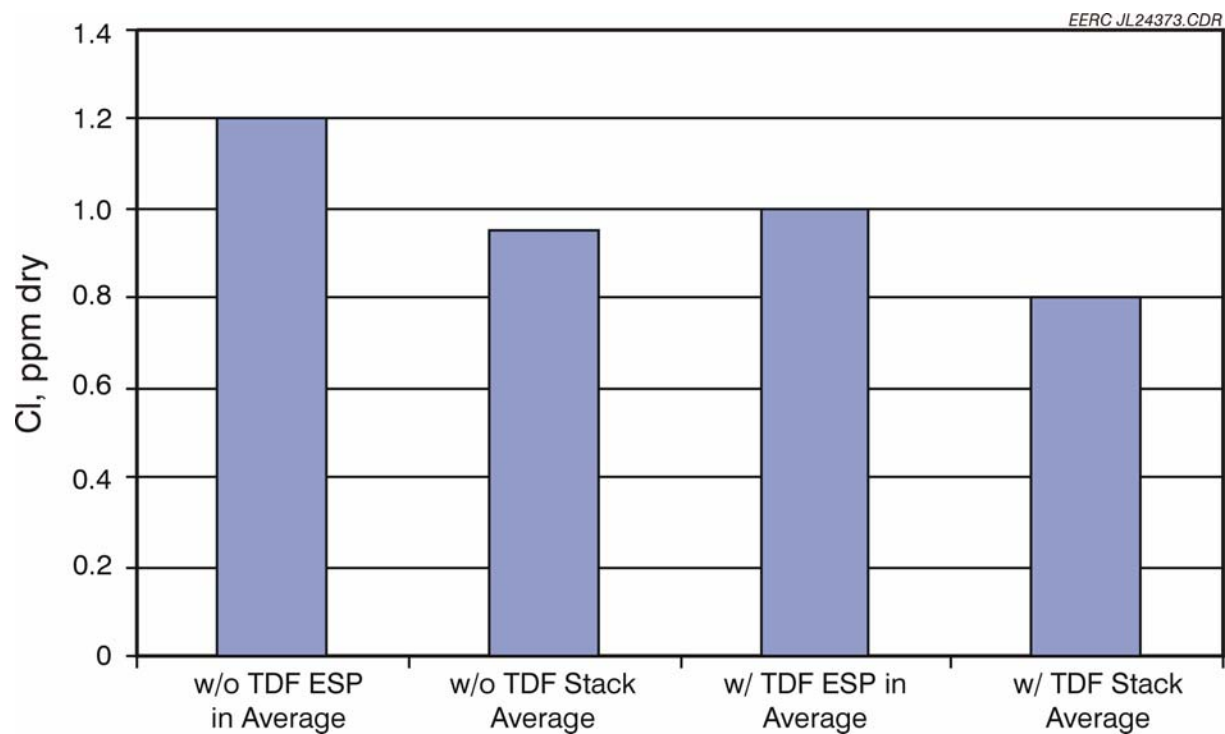
Figure 44. Chlorine data from EPA Method 26A measurements.
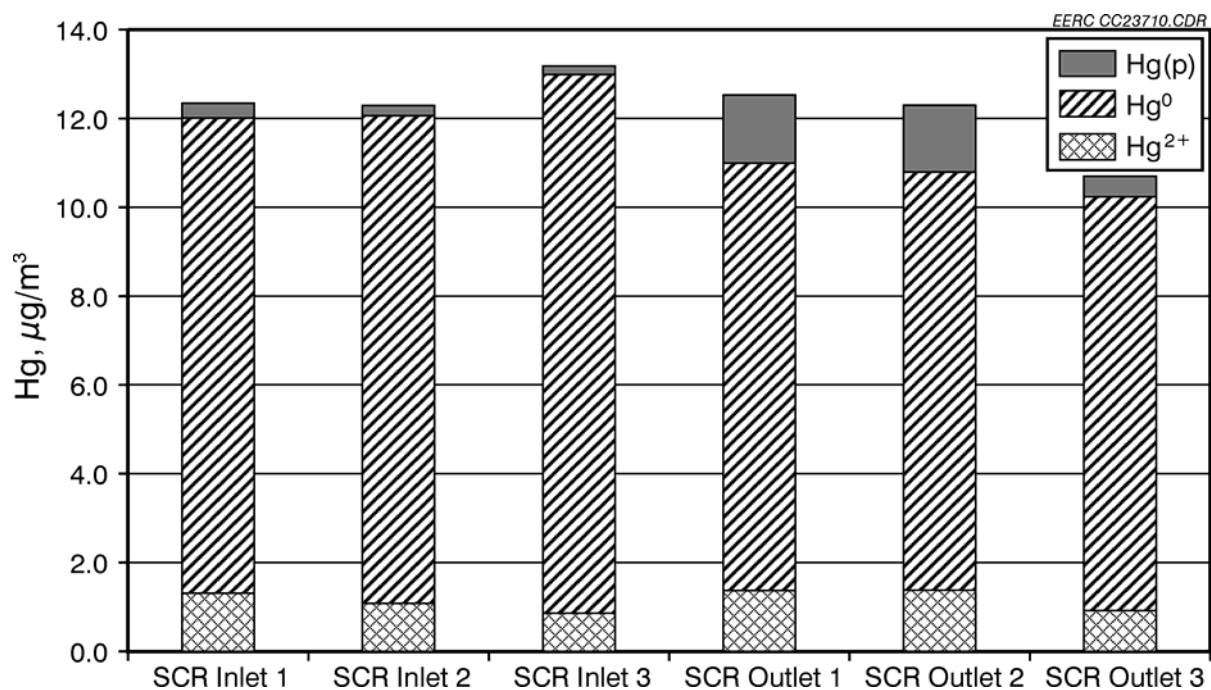
Figure 45. Mercury speciation measurement at the inlet and outlet of the SCR catalyst after exposure to flue gases and particulate for 6 months.

Elemental Hg oxidation has been observed in laboratory-, pilot-, and full-scale testing using SCR catalysts (28–30). In these studies, the metal oxides V_2O_5 and TiO_2 have been shown to promote the conversion of Hg^0 to oxidized and/or particulate-bound Hg. Full-scale tests in Europe (31) and the United States (32) have indicated that the V_2O_5 and TiO_2 catalyst may promote the formation of oxidized Hg. However, studies with low-rank fuels have shown that the ability to oxidize Hg is largely dependent on the composition of the coal (32).

Blythe and others (33) conducted Hg oxidation studies at the Coal Creek Station with multiple catalysts. The catalysts were tested downstream of an ESP and upstream of an FGD system. The compositions of the catalysts were SCR-based, carbon-based, fly ash-based, palladium-rich, and gold-rich. All of the catalysts were of honeycomb-type geometry and had a cell pitch of just over 3 mm. Of these catalysts, the palladium and carbon catalysts were the most reactive. The palladium catalyst achieved over 65% Hg oxidation after 20 months of operation, while the carbon catalyst oxidized 80% of the Hg after 13 months of operation. This technology still has some problems with an increase in pressure drop across the catalyst bed; however, the installation of acoustic horns seems to help this issue (33).

Recently, the ability of mercury to be oxidized across the SCR catalyst was investigated at the Coyote Station. The Coyote Station is fired on North Dakota lignite, and the flue gases are dominated by elemental mercury. Measurement of mercury speciation was determined using the OH method at the inlet and the outlet of the SCR catalyst. These results show limited oxidation of mercury across the SCR catalyst when firing lignite coals. The reasons for the lack of mercury oxidation include the following: there was no chlorine present in the coal and flue gas to enhance the oxidation of Hg^0 catalytically; higher levels of alkali and alkaline-earth elements acted as sorbents for any chlorine present in the flue gas, and low levels of acid gases were present in the flue gas. The active sites may also be partially blinded and therefore unable to oxidize mercury.

TASK 4 – PARTICULATE AND MERCURY CONTROL FOR NORTH DAKOTA LIGNITES USING THE *ADVANCED HYBRID*™ FILTER TECHNOLOGY

The goal of this task was to evaluate selected furnace additives and flue gas sorbent for mercury removal in a coal-fired combustion system equipped with an ESP followed by an *Advanced Hybrid*™ filter.

Experimental

The *Advanced Hybrid*™ filter, which was developed by the EERC with the support of DOE and W.L. Gore & Associates Inc., combines electrostatic precipitation and fabric filtration in the same vessel. Extensive pilot-scale testing indicates that the *Advanced Hybrid*™ filter provides high (>99.99%) particle collection efficiency with high A/C ratios and long bag-cleaning intervals with reasonable pressure drop. The *Advanced Hybrid*™ filter has unique advantages for mercury control since it provides excellent gas–solid contact in a sorbent injection application, and the gas–solid contact is expected to be further improved under a low dust-loading environment. Figure 46 shows the schematic diagram of the system. The first stage of the ESP removes approximately 90% of fly ash in the flue gas before it enters into the retrofitted *Advanced Hybrid*™ filter. Selected sorbents were fed with a K-tron dual-screw feeder downstream of the ESP before the flue gas entered into the retrofitted *Advanced Hybrid*™ filter. Both continuous and batch injection modes were tested as functions of the flue gas temperature (300° and 400°F) and injection rate. Mercury oxidants were fed into the furnace with the
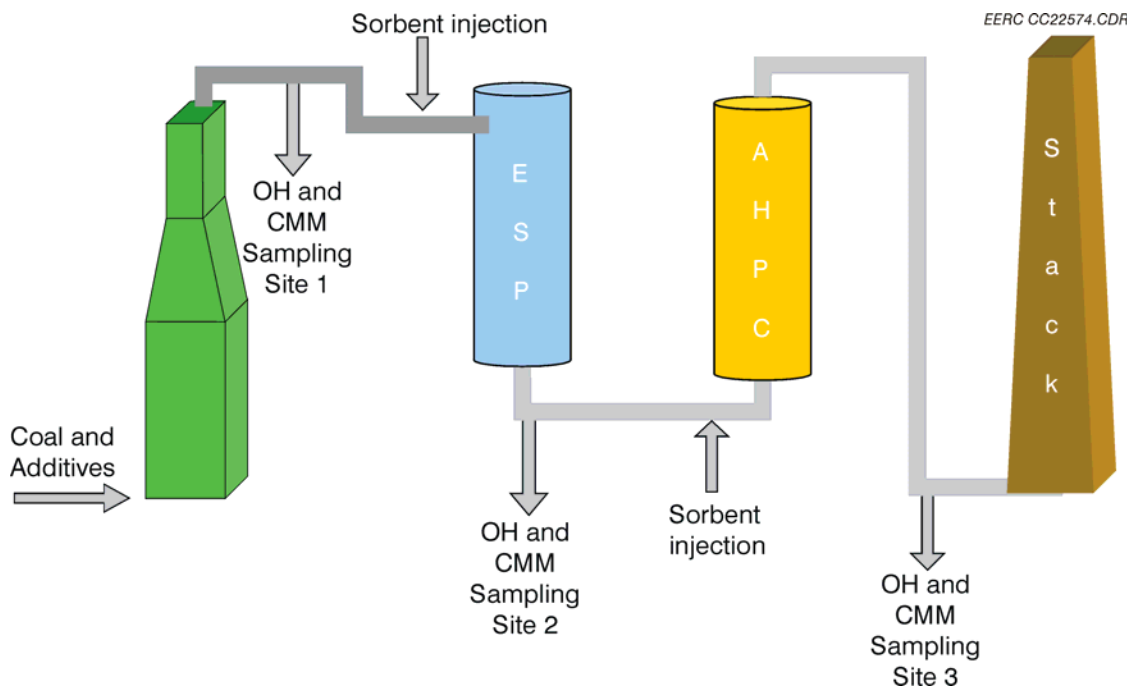
Figure 46. Injection and sampling schematic of the PTC with an ESP and *Advanced Hybrid*™ filter.

Freedom lignite. Three CMMs were used to monitor mercury vapor concentrations at the combustor outlet (Site 1) and the *Advanced Hybrid*™ filter inlet (Site 2) and outlet (Site 3) continuously during the testing period. OH method sampling was also performed to verify the CMM data. OH method measurements also provide information on particle collection efficiency for the retrofitted *Advanced Hybrid*™ filter.

The pilot-scale test using Freedom lignite was carried out from September 8, 2003, to September 19, 2003. The ADA Amended Silicate™ sorbent was not available during the test because of a product quality problem at ADA. A summary of the test matrix for this task is listed in Table 22. DARCO® FGD and regenerated FGD were tested for mercury removal from the flue gas in the *Advanced Hybrid*™ filter at 300° and 400°F with both continuous and batch injection modes. Also, mercury oxidants including NaCl, SEA2, and zinc were examined for their impacts on mercury removal.

Advanced Hybrid™ Filter Operation

The first stage of the ESP was operated at 2–3-mA corona current levels to remove 90%–95% fly ash in the flue gas. The retrofitted *Advanced Hybrid*™ filter was operated under 40–60 kV with 4-mA corona current. The A/C ratio was set at 12 ft/min. Pressure drop across the filter bags started at 2.5 in. W.C. with clean bags and slowly rose because of the particle accumulation on the bag surface. Sorbent injection prior to the *Advanced Hybrid*™ filter and mercury oxidant additions into the furnace did not cause any operating difficulties in electrostatic precipitation control or bag cleanability. Particulate matter emission out of the *Advanced*

Table 22. Test Matrix for Retrofitted *Advanced Hybrid*™ Filter

	Mercury Oxidant		Sorbent		Sorbent Injection Mode	Temperature, °F
	Category	Injection Rate, lb/Macf	Category	Injection Rate, lb/Macf		
T4-1	None	NA	None	NA	NA	300
T4-2	None	NA	DARCO® FGD	0–8.08	Continuous	300
T4-3	None	NA	DARCO® FGD	0–8.08	Batch	300
T4-4	None	NA	DARCO® FGD	0–4.59	Continuous	400
T4-5	None	NA	DARCO® FGD	2.02	Batch	400
T4-6	NaCl	0–11	NA	None	NA	300
T4-7	SEA2	0–7.34	NA	None	NA	300
T4-8	Zn–NaCl	7.34–11	NA	None	NA	300
T4-9	NaCl	3.67–7.34	DARCO® FGD	1.22–2.57	Batch/cont.	300
T4-10	None	NA	Regen.	2.2	Batch	300

Hybrid™ filter was 0–0.0002 g/scf according to the OH method dust-loading measurements at the *Advanced Hybrid*™ filter outlet, indicating an extremely high particle collection efficiency >99.9% based on the 0.148–0.22 g/scf dust loading at the combustor outlet.

Tasks 1 and 4 were commingled to produce maximum results with minimum testing days. The Freedom coal flue gas compositions and mercury levels are the same as in Task 1 and are described in Task 1.

Mercury Speciation Across the Advanced Hybrid™ Filter in Baseline Test

Test T4-1 (Baseline). During the pilot-scale test, Freedom lignite with a mean mercury content of 0.05 μg/g (dry basis) was combusted at a nominal feed rate of 87 lb/hr. The coal combustion flue gas exiting the PTC was cooled down to a designated temperature of 149°C (300°F) and was then introduced into the single-wire tubular ESP unit followed by the *Advanced Hybrid*™ filter. Three CMMs were used to monitor mercury vapor concentrations at the combustor outlet and the *Advanced Hybrid*™ filter inlet and outlet. OH method samples were collected at the three locations to verify the CMM data. The purpose of the baseline test (T4-1) was to establish speciated mercury concentrations in Freedom lignite flue gas and determine whether there were changes in mercury speciation across the overall unit. CMM and OH method measurements are plotted in Figure 47, and both methods indicate most of the mercury from Freedom lignite combustion presented as elemental vapor, with 10.9%–12.9% oxidized mercury
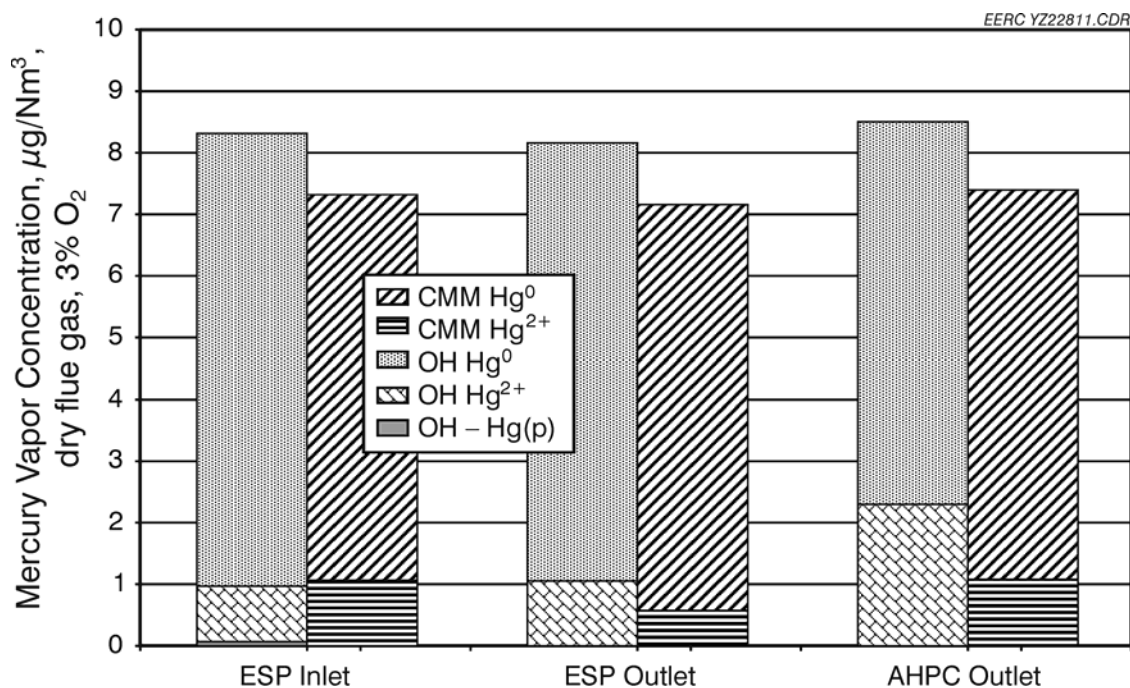
Figure 47. Mercury speciation across the ESP and *Advanced Hybrid*™ filter in Freedom coal flue gas (baseline, 300°F).

and virtually no particle-associated mercury. The total mercury concentrations at the *Advanced Hybrid*™ filter inlet and outlet are almost the same as at the combustor outlet, indicating no further mercury capture across the unit.

Mercury removal across the *Advanced Hybrid*™ filter was evaluated with sorbent injection, mercury oxidant addition, and combinations of sorbent and mercury oxidant. The sorbents were injected upstream of the *Advanced Hybrid*™ filter, while the mercury oxidants were added to the coal prior to introduction to the furnace.

Results and Discussion

Mercury Control Technology Results

Tests T4-2 to T4-3. Two tests were conducted to evaluate mercury removal in the retrofit *Advanced Hybrid*™ filter with DARCO® FGD carbon as functions of injection rate and injection mode.

Figure 48 shows typical temporal variations in mercury vapor species across the system in 300°F flue gas under a continuous DARCO® FGD injection (0.92–2.02 lb/Macf) upstream of the *Advanced Hybrid*™ filter unit. Total mercury vapor concentrations at the combustor outlet and the
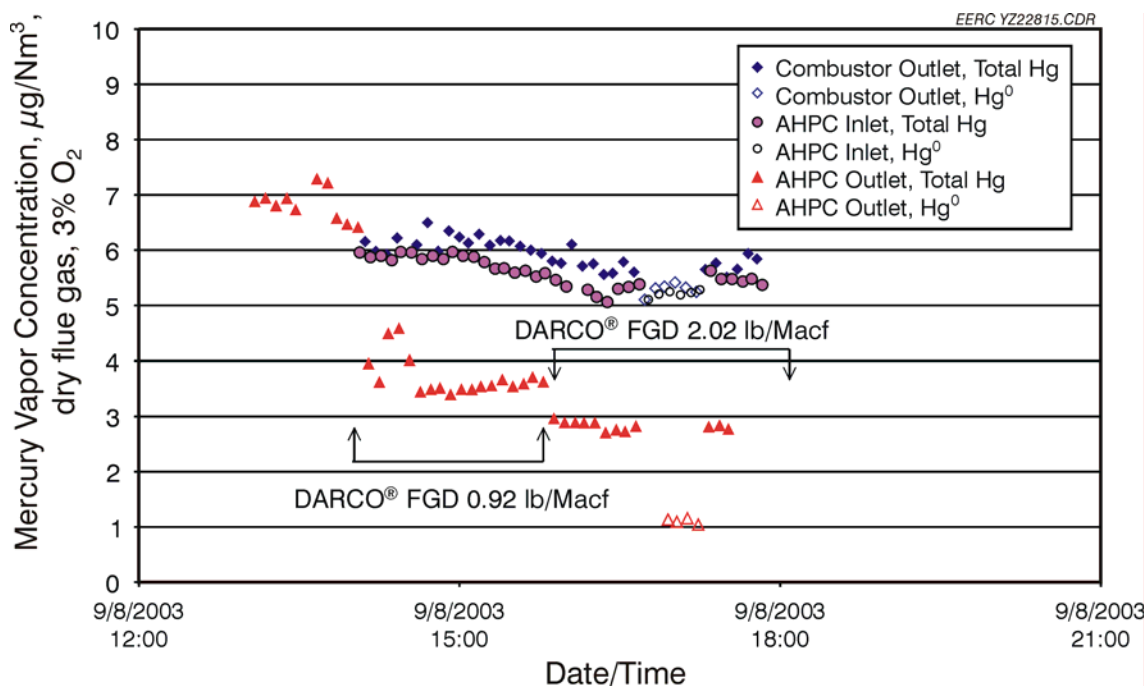
Figure 48. Mercury species across the *Advanced Hybrid*™ filter with DARCO® FGD continuous injection, 300°F.

Advanced Hybrid™ filter unit inlet were in the range of 5–7 μg/Nm^3 with elemental mercury dominating, indicating that no mercury conversion occurred before the contact with DARCO$^®$ FGD carbon. At the 0.92 lb/Macf DARCO$^®$ FGD injection rate, total mercury emissions out of the *Advanced Hybrid*™ filter decreased from the 6.7 μg/Nm^3 mercury emission at the baseline test to 3.5 μg/Nm^3. At the 2.02 lb/Macf DARCO$^®$ FGD injection rate, the total mercury vapor concentration at the *Advanced Hybrid*™ filter outlet was further reduced to 2.7 μg/Nm^3 while elemental mercury was only 1.0 μg/Nm^3, indicating DARCO$^®$ FGD carbon not only captured but also oxidized mercury. OH samples were collected at the three locations (Sites 1–3) during the 2.02-lb/Macf FGD injection phase of the test. The OH results are plotted in Figure 49, showing that mercury species concentrations at the *Advanced Hybrid*™ filter inlet are the same as at the combustor outlet and reduced to 2.4 μg/Nm^3 at the *Advanced Hybrid*™ filter outlet with 69.5% as oxidized mercury vapor. The CMM data agree very well with the OH measurement results. Mercury removals in the *Advanced Hybrid*™ filter system with continuous DARCO$^®$ FGD carbon injection are calculated and plotted as a function of injection rate as shown in Figure 50.

Test T4-3 was aimed at examining the impact of sorbent batch injection on mercury removal in the retrofit *Advanced Hybrid*™ filter. This was accomplished through mandatory power shutdowns to the *Advanced Hybrid*™ filter while each batch of carbon was injected into the flue gas in advance of the inlet to the *Advanced Hybrid*™ filter chamber. With the power off, all of the carbon was expected to be collected on the filter bag surface where the sorbent could
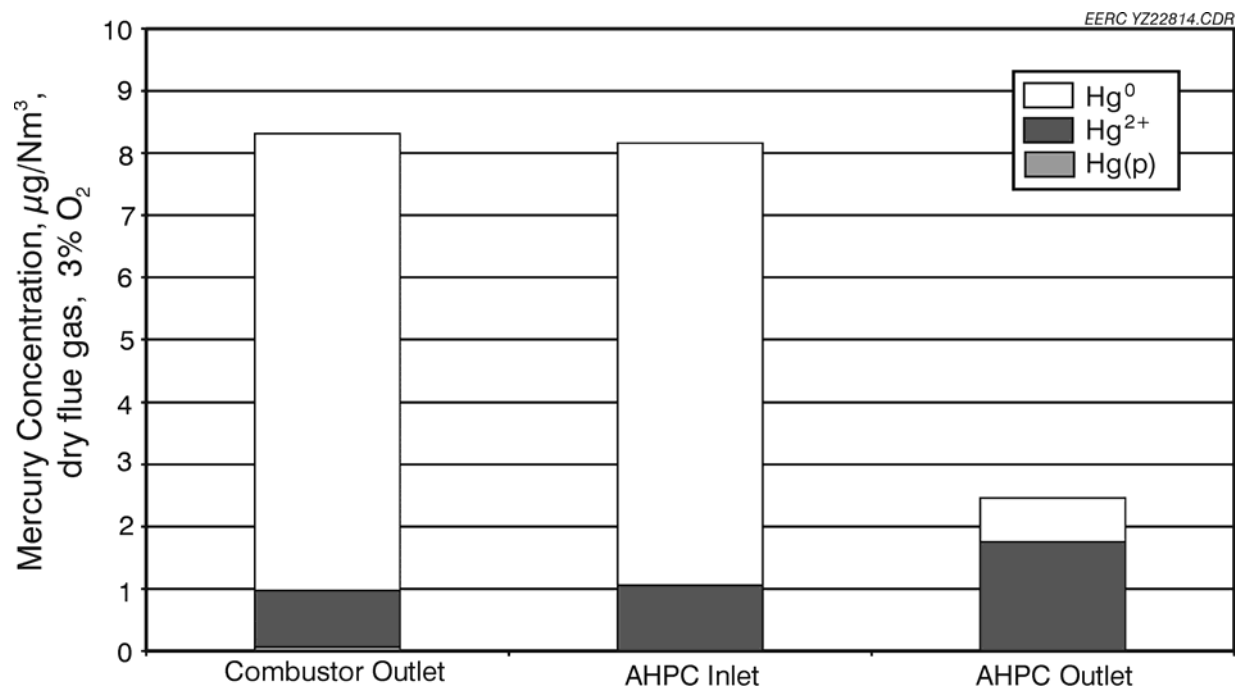
Figure 49. Mercury speciation across the retrofitted *Advanced Hybrid*™ filter with 2.02 lb/Macf DARCO$^®$ FGD injection (Freedom, 300°F).
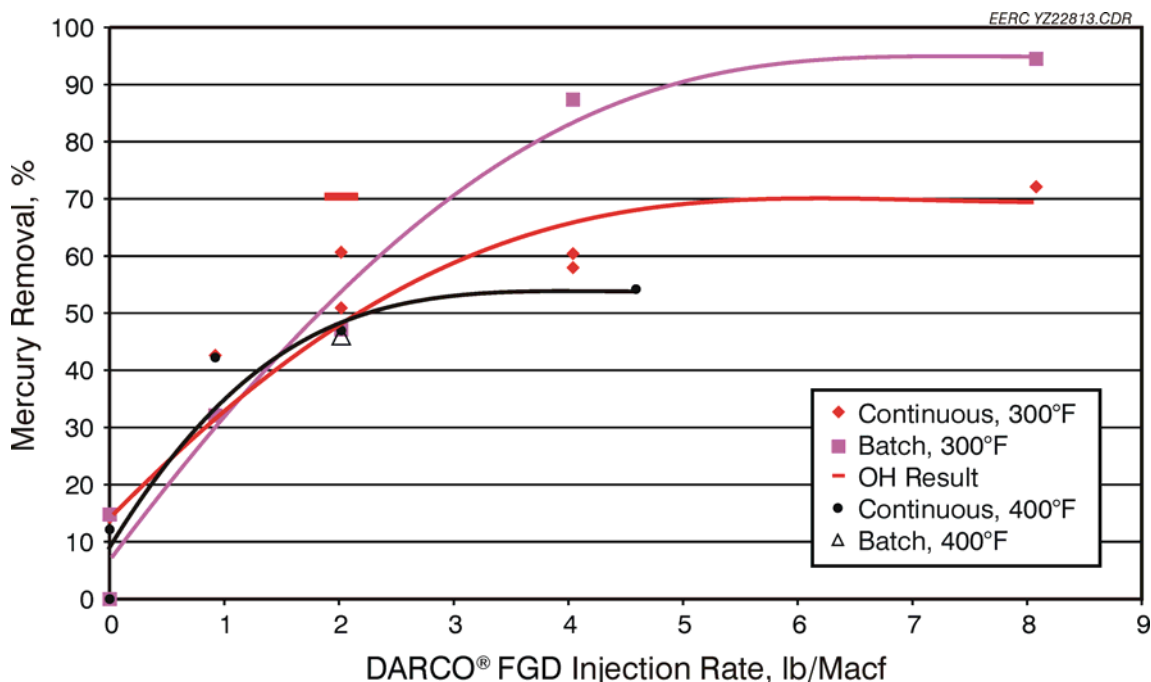
Figure 50. Mercury removal in a retrofitted *Advanced Hybrid*™ filter with DARCO® FGD injection (Freedom coal).

capture mercury most efficiently. The entire injection period lasted less than 1 minute, and then the electric power was back online. The sorbent injection rate was determined based on the amount of the sorbent batched into the system and the time interval between the batch injections.

Figure 51 shows variations in mercury emissions under batch injection mode. Before the batch injection, mercury vapor concentration at the *Advanced Hybrid*™ filter outlet was around 7.3 μg/Nm³, close to the 7.8 μg/Nm³ measured at the combustor outlet, showing no inherent mercury capture across the system in the baseline test. Five grams of DARCO® FGD carbon was batched into the flue gas in a 1-hr period, corresponding to a 0.92-lb/Macf sorbent injection rate. Total mercury vapor concentration was dramatically reduced to 2 μg/Nm³ and recovered to the baseline level within a 1-hr period before another 5-g batch was added. The lowest mercury vapor concentration during the 0.92-lb/Macf batch injection test was 2 μg/Nm³. This indicates that the sorbent reached its capacity for mercury capture in the Freedom coal flue gas and that a higher sorbent injection rate is necessary for better mercury removal. Two 11-g batches were then added into the system within a 1-hr period to equal a 4.04-lb/Macf injection rate. The mercury emission level decreased to 0.65 μg/Nm³ and recovered to 1.8 μg/Nm³ after the 1-hr test.

The batch test results plotted in Figure 52 show a 22-g DARCO® FGD injection within a 2-hr period, corresponding to a 2.02-lb/Macf injection rate. After the 22-g carbon introduction into the system, the mercury emissions immediately decreased to 0.38 μg/Nm³, then gradually increased to 10.8 μg/Nm³, higher than the inlet mercury concentration. This is probably an
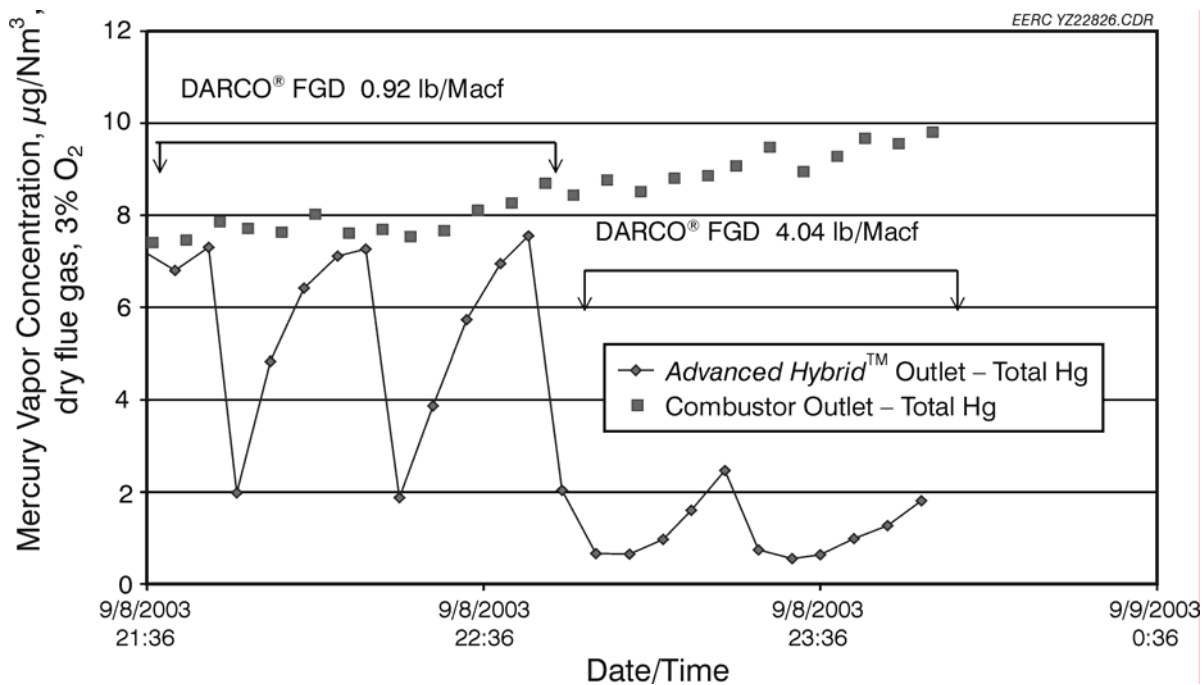
Figure 51. Mercury vapor species across the *Advanced Hybrid*™ filter under DARCO® FGD (5 g and 11 g batch injection, 300°F) for 9/8/2003.
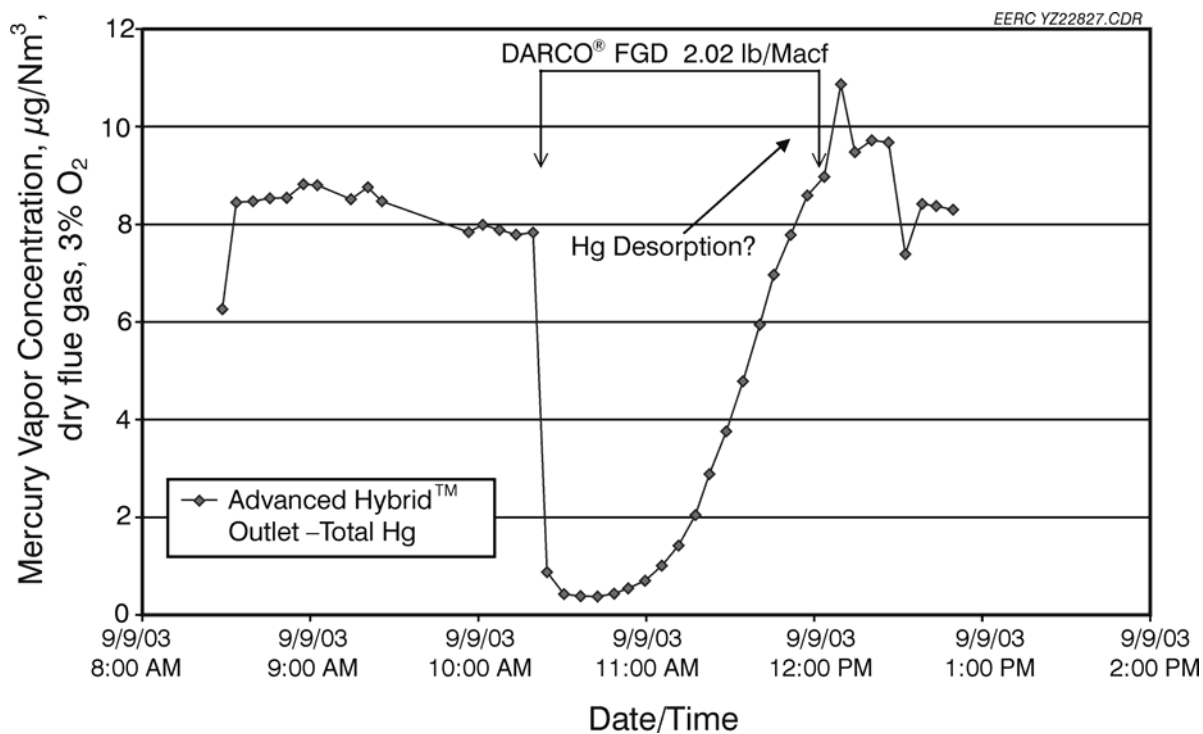
Figure 52. Mercury vapor species across the *Advanced Hybrid*™ filter under DARCO® FGD (22 g batch injection, 300°F) for 9/9/2003.

indicator of mercury desorption from the carbon sorbent after a long exposure to the flue gas. Mercury removal efficiencies were calculated based on the inlet mercury concentrations and the time-integrated average of mercury emissions and are included in Figure 50 as a function of injection rate. At injection rates up to 2 lb/Macf, mercury capture efficiency was similar for both injection modes since the DARCO® FGD carbon reached its capacity for mercury capture under the low injection rate. At injection rates above 4 lb/Macf, the batch mode outperformed the continuous mode (87.4% to 60.5% mercury removal, respectively) with the result that the carbon was most efficiently utilized on the filter bags' surface rather than on the collection plate. Doubling the sorbent injection rate increased the mercury removal by 7% and 12%, respectively, with the batch mode DARCO® FGD carbon injection reaching 94.5% at 8.08 lb/Macf.

Tests T4-4 and T4-5. Two tests were performed to evaluate mercury capture by DARCO® FGD carbon in the retrofit *Advanced Hybrid*™ filter operated at an elevated temperature of 400°F. Mercury removals by DARCO® FGD at 400°F are plotted in Figure 50. A comparison with the 300°F testing data indicates no significant mercury removal dependence on operating temperature.

Tests T4-6 to T4-8. Three tests were carried out to investigate the effect of mercury oxidants, including NaCl, SEA2, and zinc, on mercury removal in the *Advanced Hybrid*™ filter system. Figure 53 shows that with the additions of NaCl and SEA2 to the coal prior to introduction to the furnace, mercury removal efficiencies increased significantly: 47.5% at the 11-lb/Macf NaCl injection rate and 76.7% at the 7.34-lb/Macf SEA2 injection rate. As in Task 1, SEA2 has a much better performance on mercury capture than NaCl in the retrofit *Advanced Hybrid*™ filter because SEA2 (generated in the combustion zone) reacts more easily with mercury vapor and converts into particulate-associated mercury. Both the ESP and the retrofitted *Advanced Hybrid*™ filter hopper ashes were collected during the NaCl and SEA2 injection tests and analyzed for mercury, sodium, chloride, and SEA2 constituents. The results are listed in Table 23. During the NaCl and SEA2 addition tests, mercury enrichment was observed in both the ESP and *Advanced Hybrid*™ filter hopper ashes with a higher enrichment in the finer *Advanced Hybrid*™ filter hopper ash. Most SEA2 constituents were present in the larger-sized ESP ash while chlorine was well distributed between the two ashes. Figure 54 shows the impacts of metallic zinc and the combination of Zn and NaCl on mercury emission of the *Advanced Hybrid*™ filter. The addition of zinc into the furnace alone resulted in a marginal increase of mercury capture of 13.2% at 7.34 lb/Macf. The addition of zinc and NaCl had a better mercury removal than the zinc-only addition. However, in comparison with the results from NaCl addition, the metallic zinc had a negative impact on mercury capture since zinc will compete with mercury for the chlorine species.

Test T4-9. Since NaCl has shown the beneficial effect on mercury capture by enhancing reactivity between fly ash and mercury vapor, Test T4-9 was carried out to investigate mercury removal in the *Advanced Hybrid*™ unit with the NaCl–DARCO® FGD carbon combination. The benefit of simultaneous injections is a reduction in carbon usage through replacement with the more cost-effective NaCl as a mercury oxidant without causing any operating difficulty. NaCl was continuously fed into the furnace with coal while DARCO® FGD carbon was injected into the system in both continuous and batch injection modes. The data in Figure 55 show that the 3.67-lb/Macf NaCl feed rate combined with the 2.57-lb/Macf DARCO® FGD continuous
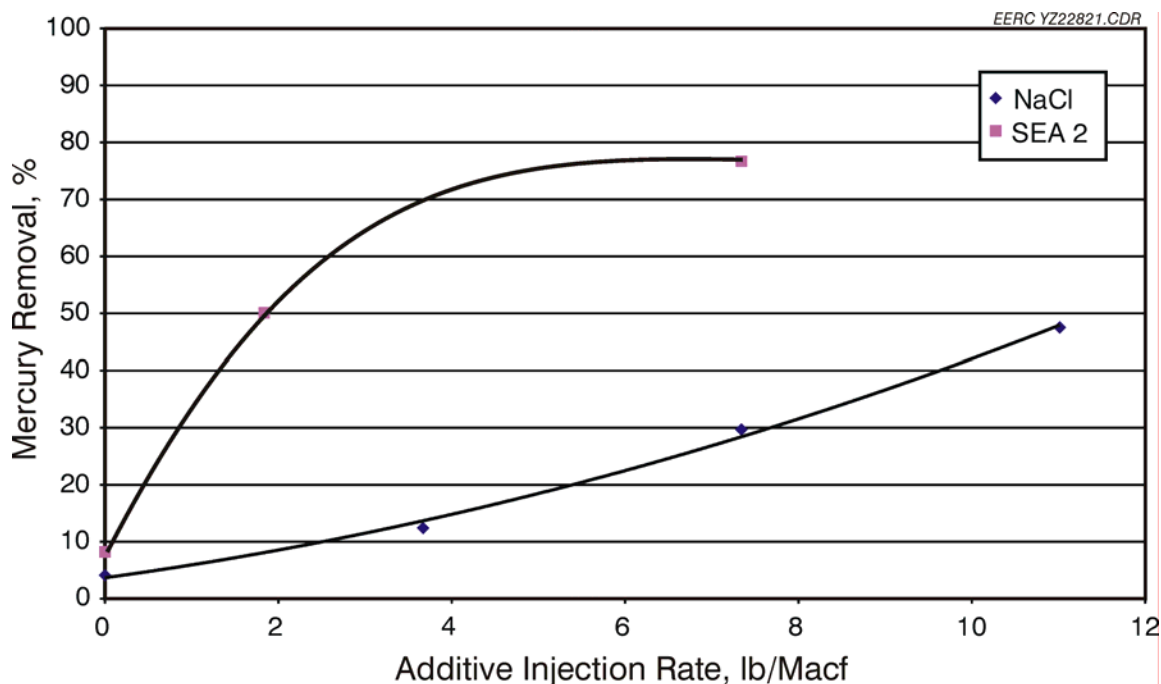
Figure 53. Effect of additives for mercury control in the *Advanced Hybrid*™ filter (Freedom coal, 300°F).

Table 23. ESP and *Advanced Hybrid* ™ Filter Hopper Ash Analyses

	ESP				*Advanced Hybrid* ™ filter			
	Cl, μg/g	SEA2, μg/g	Na, μg/g	Hg, μg/g	Cl, μg/g	SEA2, μg/g	Na, μg/g	Hg, μg/g
Baseline	206	<30	11,200	0.0139	NA			
NaCl	5440	NA	18,700	0.38	2800	NA	39,500	0.614
SEA2	NA	12,600	18,600	0.203	NA	<60	37,600	0.89

injection rate resulted in 79% mercury capture, which is an additive response from separate injections of DARCO® FGD (~56% at the 2.57-lb/Macf injection rate) plus NaCl (~12.4% at the 3.67-lb/Macf injection rate). The improved 70% mercury collection efficiency matches the mercury removal at 8.08 lb/Macf DARCO® FGD without NaCl addition. Hence, the carbon injection rate was decreased to 32% by the simultaneous NaCl addition in the furnace to yield the same effect. OH measurements show variations of mercury species across the system caused by NaCl and DARCO® FGD additions (shown in Figure 56). More particulate-associated mercury was present in the combustor outlet sample than in the baseline test as a result of the NaCl addition. The mercury removal efficiency was calculated based on the OH data, and it matches the CMM data well. Increasing the NaCl feed rate to 7.34 lb/Macf resulted in 79% mercury removal. The sum effect of NaCl and DARCO® FGD carbon was also shown in the DARCO® FGD batch injection test. With 7.34-lb/Macf NaCl and 1.22-lb/Macf DARCO® FGD added in the
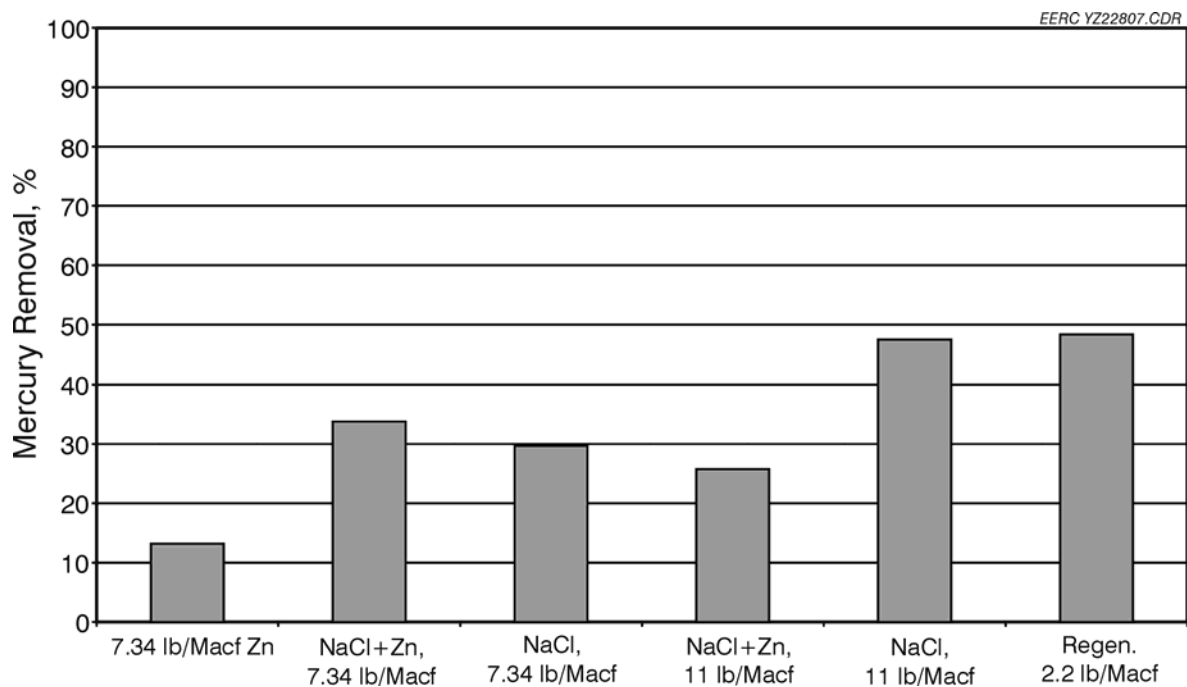
Figure 54. Effects of additives on mercury capture in a retrofitted *Advanced Hybrid*™ filter (Freedom coal, 300°F).
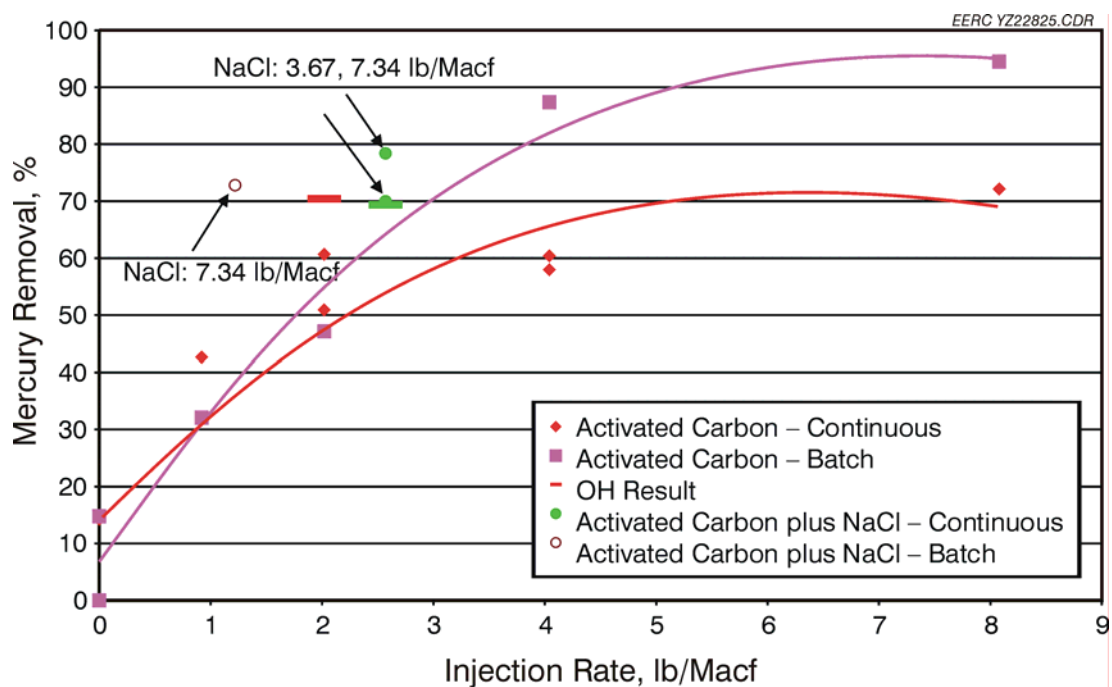
Figure 55. Mercury removal with FGD plus NaCl in the retrofitted *Advanced Hybrid*™ filter (Freedom coal, 300°F).
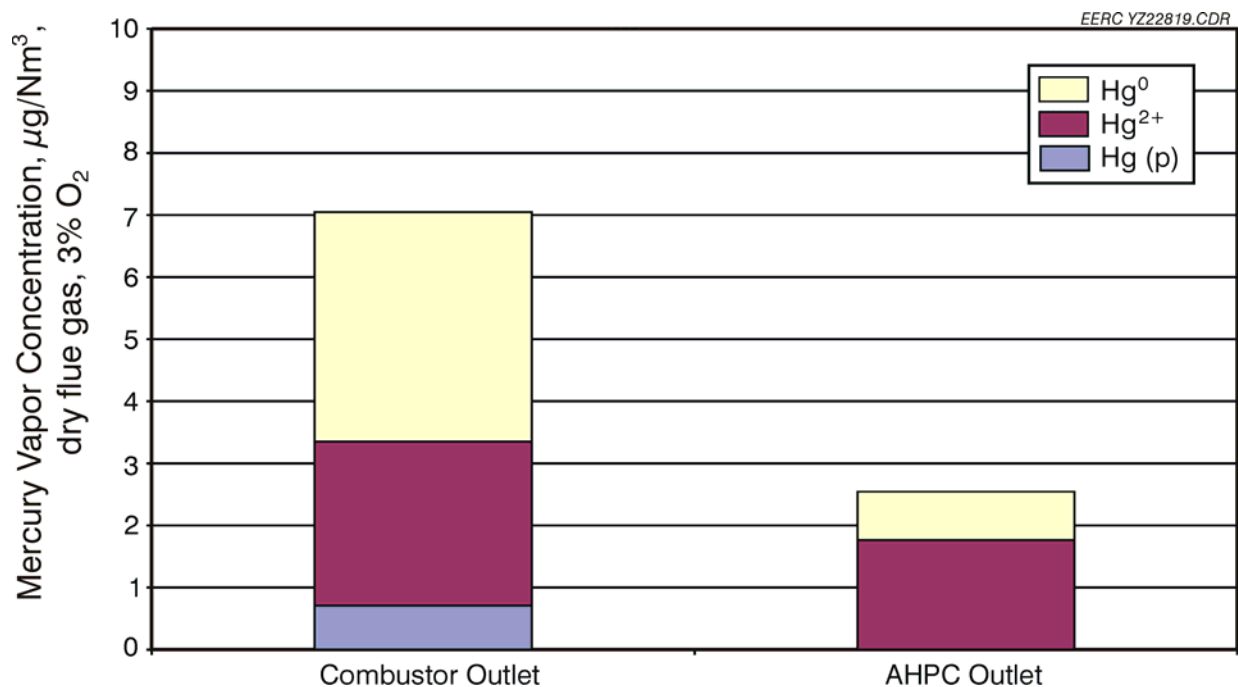
Figure 56. Mercury speciation across the retrofitted *Advanced Hybrid*™ filter with 2.57-lb/Macf DARCO® FGD plus 3.67-lb/Macf NaCl injection (Freedom coal, 300°F).

batch mode, the overall mercury removal reached 72.8%, of which ~39% represents the 1.22-lb/Macf DARCO® FGD batch injection and 30% represents the 7.34-lb/Macf NaCl addition.

The EERC has developed a regeneration process to reuse sorbent. Short-term Test T4-10 was performed to evaluate the effectiveness of the regenerated FGD sorbent on mercury capture in the *Advanced Hybrid*™ filter. Using a 2.2-lb/Macf regenerated FGD batch injection rate, the measured mercury removal was 48% (also shown in Figure 54), almost the same as the collection efficiency achieved by DARCO® FGD carbon at the same rate. More research is needed to explore this area.

TASK 5 – FIELD TESTING OF SORBENTS

The original objective of this task was to test Hg control technologies in the Advanced Hybrid™ filter insert. The task work plan included evaluation of a Gore technology consisting of a proprietary baghouse insert downstream of the FF that has shown a high potential to control Hg. However, Gore's recent decision to abandon their mercury research program has resulted in elimination of its inclusion in the task scope of work. Therefore, the objective of this task was focused on conducting slipstream baghouse testing of mercury control technologies downstream of an ESP in lieu of evaluating the Gore technology.

An existing baghouse was retrofitted, skid-mounted, transported to a power plant in North Dakota, and connected in slipstream fashion to allow for testing of actual flue gases. Additions to the existing baghouse unit for remote field application included a control room for remote operation, piping and flanges for connection to plant ductwork, a variable-speed fan, and a sorbent injection system for Hg control.

The skid-mounted baghouse was installed downstream of an existing ESP at Leland Olds Generating Station in Stanton, North Dakota. For these measurements, EPA Method 101A was used to determine the total Hg (only) removed across the baghouse system.

Experimental

Table 24 contains the experimental plan for two days of testing at the Leland Olds Station. Prior to the first day of testing, significant commissioning activities took place to ensure that the unit was operating properly and that the data were of the highest quality. North Dakota lignite coal was fired for the entire test period.

During this test period, CMMs were operated, and limited OH sampling was conducted. CMMs were installed at the ESP inlet and baghouse outlet. OH method sampling took place at the ESP inlet and the baghouse outlet. Standard quality assurance/quality control (QA/QC)

Table 24. Portable Baghouse Slipstream (Days 1 and 2) Test Matrix at Leland Olds Unit 1

Mercury Oxidant		Sorbent		Baghouse Face Velocity, ft/min
Category	Injection Rate, µg/g[1]	Category	Injection Rate, lb/Macf (g/hr)	
None	NA	None	NA	6
None	NA	DARCO® FGD	1.9 (70)	6
None	NA	DARCO® FGD	2 (100)	8
None	NA	DARCO® FGD	2 (124)	10
Chlorine	500	DARCO® FGD	0.9 (34)	6
Chlorine	500	DARCO® FGD	1 (50)	8
Chlorine	300	DARCO® FGD	2 (100)	8

[1]Chlorine added to make the µg/g equivalent in the coal.

practices were followed for all Hg sampling activities. A field spike and blank were taken during each sampling period, and all samples were collected in triplicate.

Results and Discussion

An existing pilot-scale baghouse was modified for use as a slipstream test unit. The baghouse was redesigned and modified so it could be mounted on a flatbed trailer for ease of transport and installation at any location. The slipstream baghouse chamber is designed to accommodate twelve 6-in. fabric filters, with bag lengths up to 12 ft. This equates to approximately 226 ft^2 of filtration area. To install the slipstream baghouse at a power plant, two separate 10-in. flanges are required, one at the immediate inlet location and the other downstream of this location, but upstream of any induced draft (ID) fans.

A variable-speed blower, provided as part of the mobile unit, is capable of drawing between 450 and 2700 acfm of flue gas ($\approx 300°F$) through the slipstream device for a filter face velocity between 2 and 12 ft/min. The blower is controlled at a rate sufficient to draw gases at or near the maximum system flow of 2700 acfm for all test conditions. An 8-in. baghouse bypass line is utilized as a flow control mechanism. Flow control is provided by utilization of an orifice meter on the baghouse effluent stream with a flow control valve inserted in the 8-in. bypass line. Utilization of the bypass line allows for a constant draw of flue gas, maintaining isokinetic flow at the inlet nozzle for all test conditions. In addition, pipe velocities can be maintained near 75 ft/sec for all test conditions, preventing dropout of fly ash particles. The baghouse chamber can utilize between one and three inlet ports (5-in. diameter), depending upon test conditions (see Figures 57–59). Gases are drawn from an 8-in. header at the baghouse inlet. The baghouse chamber and inlet piping runs are insulated, with heat-traced lines used to maintain temperatures above a specified minimum, assumed to be 280°F. Pictures of the portable baghouse during construction can be seen in Figures 57–61.

The baghouse was installed at Basin Electric's Leland Olds Station (Unit 1). The baghouse was mounted in slipstream fashion downstream of an existing ESP. All piping runs to the baghouse were insulated and heat-traced to ensure that the temperature did not fluctuate and thereby influence the mercury speciation. Figure 61 shows the skid-mounted baghouse installed at the Leland Olds Station.

Sorbent injection testing using the EERC trailer-mounted sorbent injection system took place for 1 week at the beginning of April 2004. DARCO® FGD was injected at various rates at the inlet to the trailer-mounted baghouse. During the weeklong test, A/C ratios were varied to achieve face velocities between 6 and 10 ft/min to investigate the effect of face velocity on mercury control. Sorbent injection was performed using a self-contained feed system, injecting sorbent into the 8-in. header at the entrance to the baghouse at rates ranging from 2 to 10 lb/Macf, depending on the level of mercury removed.

Because of commissioning problems and unstable CMM operation, only the data from the April 1 and 2 tests are included in this report. Table 25 summarizes the run conditions and flue gas concentrations for the tests conducted on April 1 and 2, 2004. The data indicate that the

Figure 57. Baghouse chamber and support structure.

Figure 58. Baghouse top and exhaust header.

Figure 59. Baghouse extension showing inlet ports.

maximum Hg removal achieved with the baghouse was near 90%, with 300 ppm Cl (coal equivalent) and 2 lb/Macf of activated carbon injection. It is interesting to note that with 500 ppm Cl and 1 lb/Macf carbon injection, the Hg removal was 67% on Day 1 of the test. The data collected on Day 2 may be showing some residual effects from injecting Cl in the system the previous day. Figure 62 shows in more detail the data from Day 2 and the effect face velocity has on Hg removal in a baghouse. The outlet Hg concentration dropped slightly as the face velocity was increased from 6 to 8 ft/min and finally to 10 ft/min. The ACI rate was increased with the face velocity to keep the carbon feed rate in lb/Macf consistent. The drop in Hg concentration was only 1–2 $\mu g/m^3$ and may not be significant. Further testing should be conducted to determine if this is a real effect.

Figures 63 and 64 contain the raw data collected on April 1 and 2 for Cl, ESP inlet Hg, baghouse outlet Hg, carbon feed rate, and baghouse flow. One can see from these figures that the baghouse operated very smoothly for the 2-day period. Figure 64 also indicates the low mercury concentration exiting the baghouse prior to the onset of carbon injection followed by a sharp increase in the baghouse outlet Hg concentration. A possible explanation for this is that the residual carbon and chlorine on the bags captured mercury. This equilibrium was upset when carbon injection commenced, thereby causing the mercury to be released.
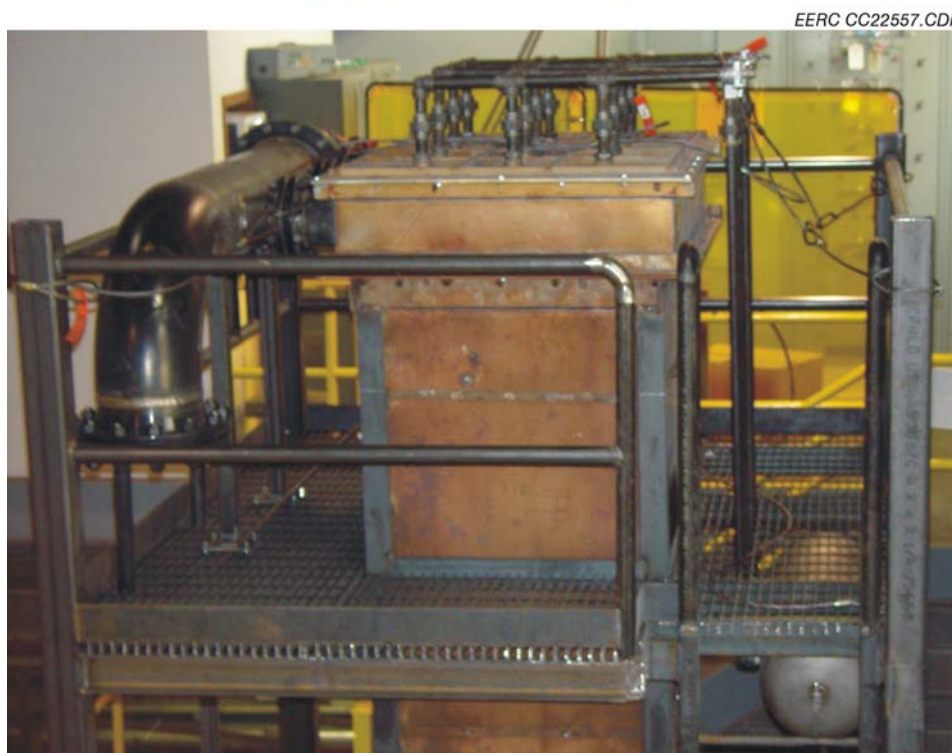
Figure 60. Completed baghouse.

Task 5

Figure 61. The portable baghouse unit installed at Basin Electric's Leland Olds Station for sorbent injection field tests.

Table 25. Data from Leland Olds Baghouse Sampling

Run Conditions	Day 1 (April 1)			Day 2 (April 2)		
Face Velocity, ft/min	6	7.93	7.86	5.9	7.9	10.0
BH Temperature, °F	340	340	340	340	340	340
BH Flow, acfm	1342	1794	1777	1340	1793	2265
Chlorine (coal equivalent), ppm	500	500	300	0	0	0
Carbon, g/hr	34.28	49.93	99.86	69.4	98.31	124
lb/Macf	0.9282	1.014	2.06	1.90	2.01	2.01
Hg, ESP inlet, $\mu g/m^{3*}$	9.0	8.4	8.8	9.6	9.5	9.5
O_2, average %	3.9	3.9	3.9	3.9	3.9	4.0
Hg, BH outlet, $\mu g/m^{3*}$	3.0	2.76	1.27	2.9	2.1	2.1
O_2, average %	5.25	5.25	5.30	6.0	6.0	6.0
Average Hg Reduction, %	67	67	86	70	78	78

* Corrected to 3% O_2.
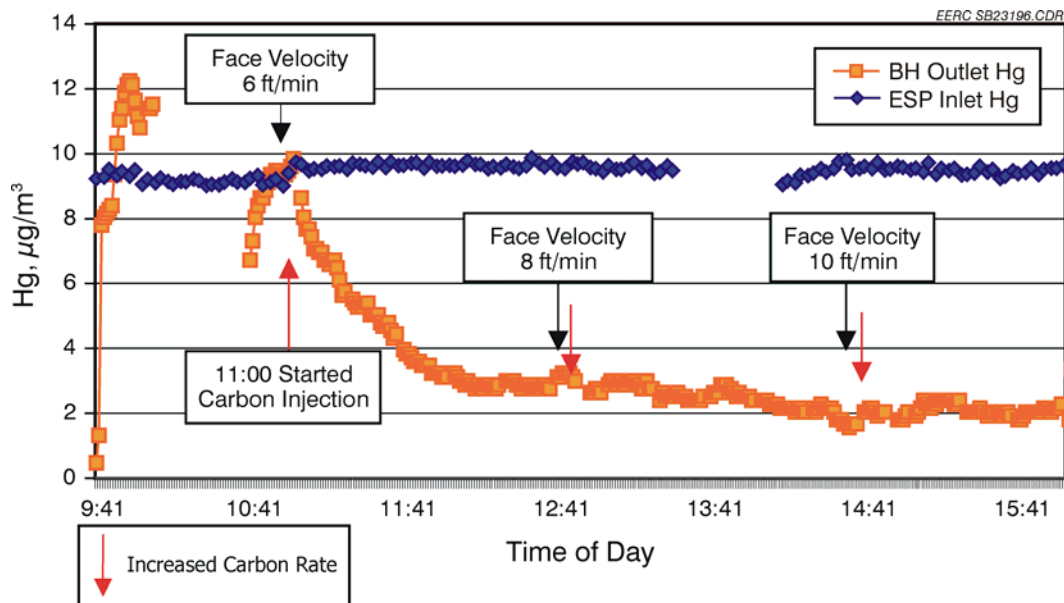
Figure 62. Mercury levels in the flue gas on Day 2 (April 2), with increasing carbon injection rate to maintain a 2-lb/Macf carbon injection rate in the baghouse while increasing the A/C ratio (face velocity).
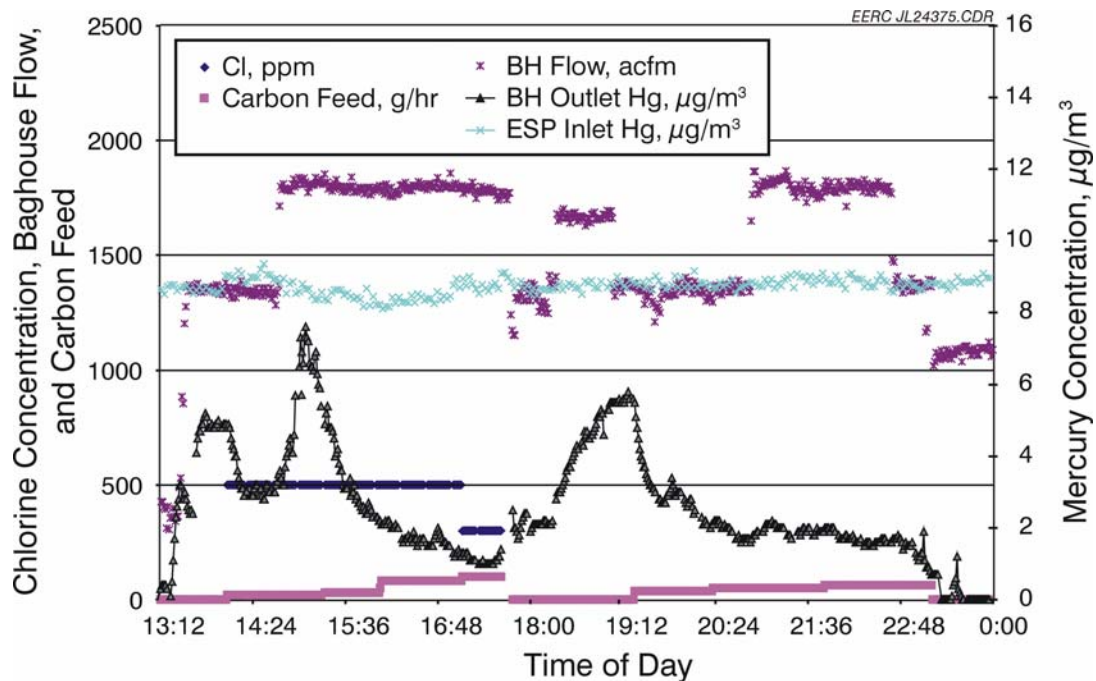
Figure 63. Raw data from Day 1 (April 1) testing at Leland Olds.
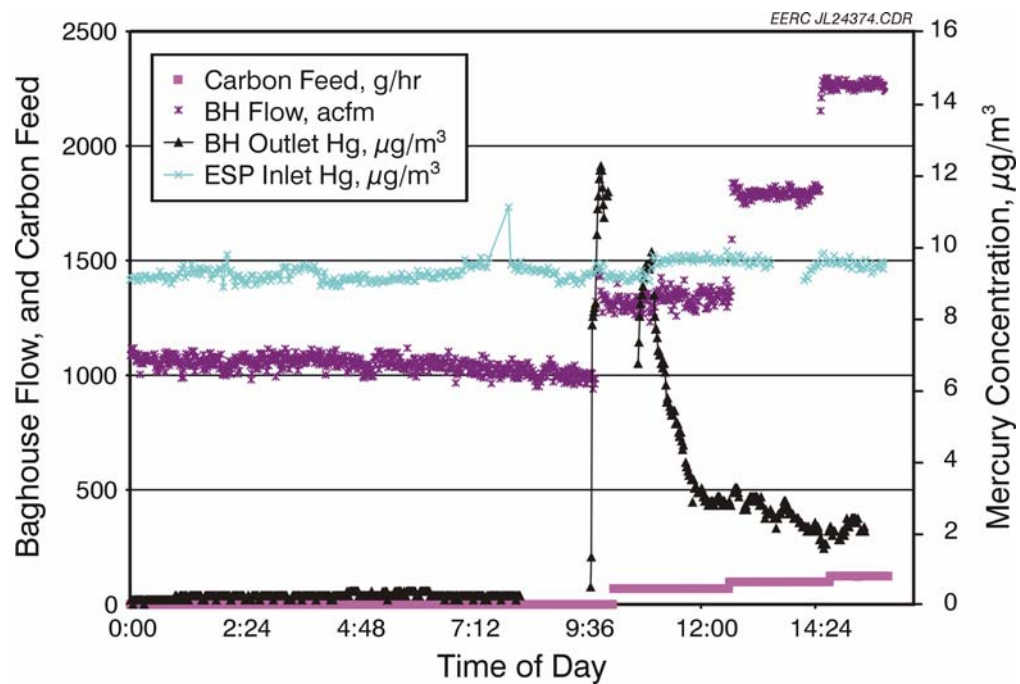
Figure 64. Raw data from Day 2 (April 2) testing at Leland Olds (no chlorine injection).

Task 5

CONCLUSIONS

Task 1 – Mercury Control Enhancement for Unscrubbed Systems Equipped with ESPs

Pilot-scale tests were performed using sorbent injection and mercury oxidant addition to evaluate their effectiveness on mercury emission control in a lignite-fired power system equipped with an ESP. The sorbents, including DARCO® FGD carbon, HCl-treated FGD carbon, EERC-treated FGD carbon, and ALSTOM enhanced FGD carbon, were injected upstream of the ESP. Different additives were introduced into the furnace with the coal to examine their impacts on sorbent performance for mercury capture.

- The baseline test results show 88.2% of Hg^0, 10.9% of Hg^{2+}, and less than 1% of particulate-associated mercury in the Freedom lignite flue gas and virtually no mercury speciation change or inherent capture across the ESP.

- DARCO® FGD carbon injection can oxidize and capture mercury with 51.5% efficiency at 4.59 lb/Macf and reached 67.2% at the elevated 18.4 lb/Macf injection rate.

- Both mercury oxidants NaCl and SEA2 have a positive mercury removal effect on the Freedom coal flue gas in the ESP configuration by enhancing mercury vapor reactivity with fly ash and in-flight DARCO® FGD carbon.

- Mercury removal efficiency reached 67.5% with 4.57 lb/Macf DARCO® FGD injection combined with 3.67 lb/Macf NaCl injection, the same as the level achieved in the 18.4 lb/Macf DARCO® FGD carbon injection alone.

- SEA2 is three times as effective as NaCl for enhancing reactivity between mercury vapor and fly ash and significantly improves DARCO® FGD performance for mercury capture, reaching 76.1% under a 2.57 lb/Macf SEA2 injection rate in combination with a 2.57 lb/Macf DARCO® FGD injection rate.

- The treated FGD carbon greatly increased mercury removal efficiency in the Freedom lignite flue gas for the ESP configuration. Lower feed rates of the treated FGD carbon were required to attain higher mercury collection efficiencies as compared to those observed with untreated DARCO® FGD sorbent.

- The ALSTOM sorbent performed very well in the ESP configuration, with one sorbent achieving over 90% mercury removal at an injection rate of <2 lb/Macf.

Task 2 – Mercury Oxidation Upstream of Dry Scrubbers

Three potential Hg sorbents (DARCO® FGD, Amended Silicate™, and EERC-treated FGD) and three Hg^0 oxidation and sorbent enhancement additives (SEA1 [NaCl], SEA1 [CaCl$_2$], and SEA2) were evaluated in the PTC equipped with a SDA–FF. A Center lignite coal was

burned in the unit while Hg(g) concentrations were measured using CMMs at the SDA inlet and FF outlet to evaluate Hg removal performance.

- Using the Hg and Cl contents of the Center lignite, the levels in the combustion flue gas were calculated to be 13.8 $\mu g/Nm^3$ and 1.59 ppmv, respectively (on a dry flue gas at 3.0% O_2 basis). The baseline measured values determined using standard methods and the CMM ranged from 12 to 13 $\mu g/Nm^3$ at the SDA–FF inlet. The initial baseline removal of mercury without additives or sorbents was found to be 2.5%. Tests at a later time during the SDA–FF testing showed higher baseline removal rates of up to 18% because of residual oxidants or sorbents that were difficult to remove from the FF.

- Mercury Sorbent Performance

  - DARCO$^®$ FGD Activated Carbon. The Hg(g) removal efficiency when injecting activated carbon upstream of the SDAA improved with increasing injection rates until it approached about 60% at an injection rate of 7.35 lb/Macf.

  - EERC-Treated FGD. The EERC-treated FGD provided very good Hg(g) capture of over 80%, even at a low injection rate of 1.84 lb/Macf. Increasing the injection rate to 3.67 lb/Macf slightly improved SDA–FF Hg(g) capture.

  - Amended Silicate™. Hg(g) removal efficiencies during the Amended Silicate™ injection averaged 74.9% and were highly variable as evidenced by a 95% confidence limit of 9.1%. The effectiveness of Amended Silicate™ to capture Hg(g) was probably enhanced by the presence of residual Cl in the system. After the injection of Amended Silicate™, the SDA–FF Hg(g) removal efficiency gradually returned to the level attained prior to testing the Amended Silicate™.

- Hg^0 Oxidation and Sorbent Enhancement Additive Performance

  - SEA1 (NaCl). The addition of NaCl to the Center lignite did not significantly increase the level of oxidized mercury. The removal efficiency across the SDA–FF was 23.5% with 3.67 lb/Macf of NaCl added and increased to 27.8% at 11 lb/Macf.

  - SEA1 (NaCl) and DARCO$^®$ FGD. With the addition of 3.67 lb/Macf of NaCl into the Center lignite coal and injection of DARCO$^®$ FGD into the combustion flue gas, the Hg(g) capture and subsequent SDA–FF removal efficiency was found to be 70%. Increasing the level of NaCl up to 11 lb/Macf and keeping the DARCO$^®$ FGD constant, the removal efficiency approached 90%. The combination of NaCl addition and DARCO$^®$ FGD injection is very effective in capturing Hg(g) in the SDA–FF pollution control devices.

  - SEA1 (CaCl$_2$). Increasing addition rates up to 11 lb/Macf, the CaCl$_2$ additions alone caused Hg(g) and Hg^0 levels to gradually decline from over 14 to 8.3 $\mu g/Nm^3$.

- SEA1 (CaCl2) and DARCO® FGD. Injection of DARCO® FGD at a rate of 3.67 lb/Macf with 11 lb/Macf CaCl$_2$ addition to the coal resulted in 80% Hg(g) removal across the SDA–FF. The SDA–FF Hg(g) removal efficiencies observed clearly demonstrate that the combination of CaCl$_2$ addition and DARCO® FGD injection provides much more effective Hg(g) emissions control relative to CaCl$_2$ addition or DARCO® FGD injection alone.

- SEA2. The addition of SEA2 alone to the coal at a rate of 3.67 lb/Macf resulted in about 80% removal across the SDA–FF.

- SEA2 and DARCO® FGD. The combination of DARCO® FGD injection at 1.84 lb/Macf and SEA2 addition provided exceptional SDA–FF Hg(g) capture, >90%, even at the lower addition rate of 1.84 lb/Macf.

Task 3 – Field Tests to Determine Impacts of Oxidizing Agents on Mercury Speciation

OH Method Hg measurements were taken at the inlet and outlet of the ESP at the Heskett Station, with and without cofiring TDF. Approximately 100 tons of TDF was delivered from Auburndale Recycling and fired at a level of 10% on a heat basis. The TDF had a heating value of over 15,000 Btu/lb and contained 324 ppm chlorine. The amount of Hg removed increased from 50% without TDF to 80% while firing TDF. The chlorine added by the TDF is likely responsible for the increase in Hg capture. Flue gas chlorine measurements taken during the same sampling period indicated that the level of chlorine in the flue gas was higher without TDF. This may indicate that the extra chlorine was captured by calcium compounds that are present in the fly ash or bed material. More work should be conducted to support or disprove this hypothesis.

Previous studies conducted with SCR catalysts on lignite-fired systems indicate that oxidation of Hg across an SCR is challenging. Other research has shown that specific metal oxides of vanadium and titanium are responsible for Hg oxidation across SCR catalysts. However, the oxidation of Hg will be highly dependent on the coal that is being fired. Heavy metal oxidation catalysts have also been studied downstream of an ESP. The results of this study indicate that palladium and carbon-derived catalysts oxidized 65% and 80% of the Hg after 20 and 13 months, respectively.

Task 4 – Particulate and Mercury Control for North Dakota Lignites Using the *Advanced Hybrid*™ Filter Technology

Pilot-scale tests were performed using sorbent injection and mercury oxidant addition to evaluate their effectiveness on mercury emission control in a lignite-fired power system equipped with an ESP followed by an *Advanced Hybrid* ™ filter. The sorbents including DARCO® FGD carbon and regenerated FGD carbon were injected upstream of the ESP in continuous and batch injection modes in 300° and 400°F flue gas environments. Different additives were introduced into the furnace with the coal to examine their impacts on sorbent performance for mercury capture.

- The baseline test results show the mercury in the Freedom lignite flue gas to be 88.2% elemental (Hg^0), 10.9% oxidized (Hg^{2+}), and less than 1% particulate-associated mercury, and virtually no inherent mercury capture across the retrofit *Advanced Hybrid*™ filter.

- At the injection rate of <2 lb/Macf of DARCO® FGD carbon, continuous and batch injection modes showed the same level of mercury capture, reaching approximately 50%–60% capture at 2.02 lb/Macf. For higher DARCO® FGD carbon injection rates of >4 lb/Macf, batch injection had a better mercury capture performance than the continuous mode since the DARCO® FGD carbon surface was more fully utilized.

- DARCO® FGD carbon showed no significant temperature dependence on mercury removal in the retrofit *Advanced Hybrid*™ filter.

- Both mercury oxidants NaCl and SEA2 have positive mercury removal effects in the Freedom coal flue gas in the *Advanced Hybrid*™ filter configuration by enhancing mercury vapor reactivity with fly ash. The addition of metallic zinc into the furnace was not effective in capturing mercury, and it deteriorated NaCl performance for mercury removal in the retrofit *Advanced Hybrid*™ filter.

- The combination of NaCl–DARCO® FGD injection significantly improved mercury removal in the retrofit *Advanced Hybrid*™ filter by attaining higher mercury collection efficiency with reduced DARCO® FGD injection rate for both continuous and batch injections. Mercury collection efficiency reached 70.0% using 2.57 lb/Macf DARCO® FGD (continuous injection) combined with 3.67 lb/Macf NaCl injection, the same as the level achieved in the 8.08 lb/Macf DARCO® FGD carbon injection.

- The regenerated FGD carbon showed encouraging rates of effective mercury removal across the retrofit *Advanced Hybrid*™ filter with batch injection in the 300°F flue gas environment, reaching 48% mercury collection at the 2.2-lb/Macf injection rate.

Task 5 – Field Testing of Sorbents and Gore Technology

A trailer-mounted baghouse was successfully designed and constructed. The baghouse was mounted on a flatbed trailer for ease of transport and installation at any location. The slipstream baghouse chamber is designed to accommodate twelve 6-in. FFs, with bag lengths up to 12 ft. This equates to approximately 226 ft^2 of filtration area. To connect the slipstream baghouse to the appropriate location at the boiler, two separate 10-in. flanges are required, one at the immediate inlet location and the other downstream of this location but upstream of any ID fans.

The baghouse was successfully installed in slipstream fashion at Basin Electric's Leland Olds Station in April 2004. Two days of carbon injection testing was completed while burning North Dakota lignite coal. The highest Hg removal achieved was near 90% with 300 ppm Cl equivalent added to the coal and 2 lb/Macf DARCO® FGD carbon injected. The effect of face velocity on Hg removal was also tested. The results of this study indicate that a small increase in Hg removal is detected as the face velocity is increased; however, further testing should be done to determine if the effect is real. A residual removal effect was observed on Day 2. The Cl added

to the coal on Day 1 seemed to enhance the removal of Hg well into the second day of testing. The Gore Technology was not included in the testing since Gore decided not to continue the development of mercury control technologies. Therefore, testing focused on sorbent injection.

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